

AN INVESTIGATION OF SUCROSE

by the METHODS of

X-RAY CRYSTALLOGRAPHY

Thesis for the Degree of Ph.D.

submitted by

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May 1946.

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INTRODUCTION.

The chemical structure of most sugars has been established beyond the possibility of doubt, owing to the work of Haworth, Hirst and their collaborators. One chemical structure may, however, comprise several geometrical possibilities, even when assumptions are made regarding bond lengths and angles. The geometrical structure of the molecules has considerable bearing on many of their physical and chemical properties and may be expected to throw light on the structure of polymerides such as starch and cellulose which are of immense practical importance, while the conformations of the pyranose and furanose rings, which are of general occurrence in sugars and sugar derivatives, are of great interest from the point of view of strain theory. Furthermore the hardness, high density and high melting point of the sugars suggest that the crystal structure of a sugar is completed by hydroxyl groups which associate to the greatest possible extent and link the molecules in all directions in the lattice. Details of the arrangement of molecules in the crystal may therefore be expected to advance considerably the knowledge of the nature and extent of co-ordination or dipole association between hydroxyl and other groups. The

sugars and their derivatives therefore merit close study by X-ray methods.

The detailed analysis of carbohydrate structures is beset by many difficulties however. The wide choice of molecular conformations, absence of outstandingly strong reflection intensities, asymmetry of the compounds concerned and lack of assistance from optical or magnetic properties of the crystals intensifies the difficulties of determining even the approximate arrangement of the molecules. It is therefore not surprising to find that although much has been published concerning the space groups and unit cell dimensions of sugars, together with a considerable amount of speculation as to the molecular conformations consistent with these observations, the structure of only one sugar derivative - glucosamine hydrobromide - has been completely determined.

Cox, Goodwin and Wagstaff⁽¹⁾ surveyed the data available for over sixty sugars and their methyl derivatives and arrived at certain conclusions, based on unit cell dimensions only, as to the nature of the pyranose and furanose rings. The pyranose ring consists of five carbon atoms and one oxygen atom, and several alternative arrangements of these atoms have been advanced. In Figs. 1.1 and 1.2 are represented two strainless forms proposed by Sachse in

which the tetrahedral interbond angles for the carbon valencies are preserved while Fig. 1.3 shows a suggested form with all five carbon atoms in a plane but with the oxygen atom displaced out of this plane.

These figures are taken from the paper by Cox, Goodwin and Wagstaff.

Fig. 1.1

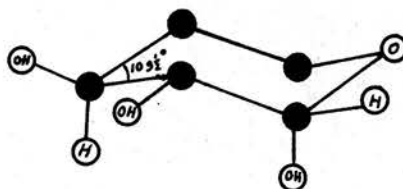


Fig. 1.2

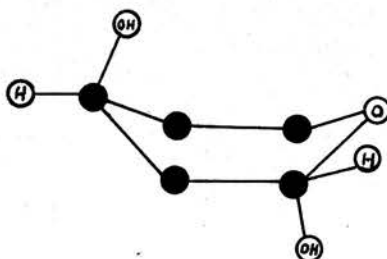
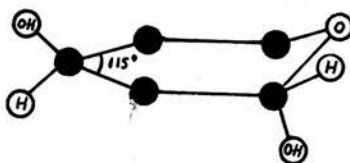


Fig. 1.3



The main interest of the problem of the pyranose ring conformation lies in the fact that a comparatively small change in the shape of the ring may be accompanied by considerable alteration in the extra-cyclic valency directions, so that the molecular form of a pyranose polysaccharide for instance is largely determined by the conformation of the rings of the monose residues. The essential difference between the Sachse models, on the one hand, and the flat structure on the other, lies in the thickness of the molecule. Of the pyranoses based on a strainless ring some, at least, must have hydroxyl groups projecting considerably from the plane of the ring. Thus the structure of β - glucose, Fig. 2.1, based on the trans or "chair-shaped" form of the Sachse ring, is nearly flat, but in that of galactose, Fig. 2.2, the hydroxyl group attached to carbon atom 4 projects about 1.5 A. from the plane of the molecule.

Fig. 2.1

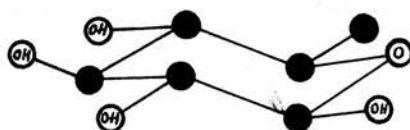
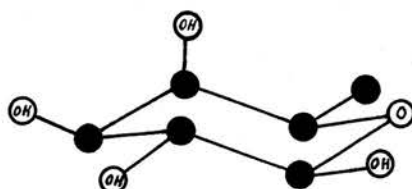


Fig. 2.2



As a result of their survey Cox and his collaborators found that in a whole series of sugars and their derivatives one cell dimension of about 4.5 A. is consistently observed, and there is no distinction between pyranoses with thick and thin molecules since this almost constant distance is too small to correspond to anything but the thickness of the molecule. This fact appears to be in agreement with a flat pyranose ring and to be incompatible with either form of Sachse ring, since in the flat ring the extracyclic valencies of carbon atoms 2, 3 and 4 are symmetrical about the plane of the ring while those of carbon atoms 1 and 5 are rotated from the symmetrical position by an amount depending on the displacement of the ring oxygen atom from the plane of the ring carbon atoms. The groups attached to carbon atoms 1 and 5 will project respectively more or less than similar addenda on the other carbon atoms according as the addenda to carbon 1 and carbon 5 are trans or cis to the ring oxygen atom, but in either case the variation from one sugar to another in the amount of projection of the hydroxyl groups will be considerably less than would be found with a Sachse-based conformation, where all the hydroxyls may be either practically in the mean plane of the ring or about 1.5 A. out of it, according to the conformation

of the ring and the configuration of the sugar concerned. The examples of β -glucose and galactose have already been mentioned. Reasons were adduced for supposing that the flat ring exists also in solution and the flat conformation was shown to account satisfactorily for various chemical reactions, such as the formation of acetone compounds.

Later, however, the positions of all the atoms (other than hydrogen) in the crystal lattices of α -chitosamine hydrochloride and hydrobromide were determined by Cox and Jeffrey.⁽²⁾ The structure deduced rests on no other assumptions than the observed isomorphism of these substances, and the pyranose ring was found to be, not of the flat form, but of the Sachse trans form. This emphasises the point that too great a reliance should not be placed on results based entirely on determinations of the symmetry and dimensions of the unit cell, but leaves unexplained the constancy of one cell dimension in a series of compounds. *remains to be explained by a more detailed knowledge of the molecular packing.*

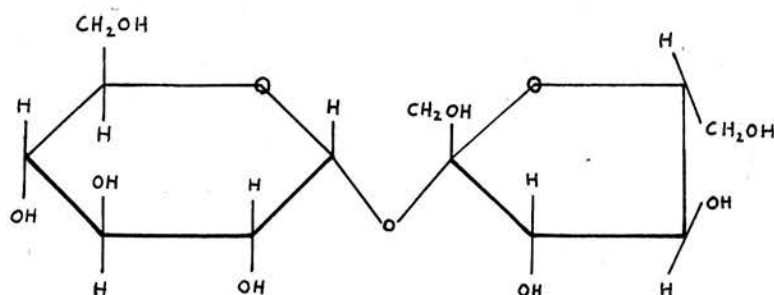
Evidence as to the conformation of the furanose ring is even more lacking, but it has been generally assumed that the four carbon atoms and one oxygen atom which comprise the ring are coplanar, since the interbond angle of this arrangement is 109° , a close approximation to the tetrahedral value. Cox and his

collaborators for instance refer to the furanose ring as "undoubtedly flat." α -methylmannoside is dimorphous and exists in pyranose and furanose forms, evidence has been brought forward by Cox and Goodwin⁽³⁾ which appears to support the view that in both cases the rings are flat. Direct evidence has hitherto been entirely lacking.

The above results and remarks apply chiefly to monosaccharides and their derivatives, the structure of disaccharides and polysaccharides is of even greater interest since the question of the mode of linking of the monose residues arises.

The structure of sucrose is of especial interest for the following reasons:-

- (a) One half of the molecule is based on a pyranose ring, the other half on a furanose ring. A complete analysis would therefore give information concerning both rings.
- (b) The chemical evidence that sucrose consists of glucose and fructose residues linked by an oxygen atom is conclusive, but there is no direct evidence as to whether they are of the α or β configurations. Indirect evidence favours the α configuration for the glucopyranose residue and the ~~configuration~~ β configuration for the fructofuranose residue, so that sucrose should probably be represented by the formula



X-ray analysis appears to be the only method capable of supplying direct evidence regarding the configurations of the two asymmetric centres involved in the linkage.

- (c) A complete determination of the structure might disclose why it has not been found possible to synthesise sucrose.

The difficulties which have prevented a complete analysis of the crystal structure of even the simplest sugars have already been mentioned. A brief account will now be given of methods which have been successfully applied in the X-ray analysis of other complex organic structures.

GENERAL X-RAY METHODS.

From the positions of the diffracted beams observed when a beam of monochromatic X-rays interacts with a crystal it is possible to determine the lengths of the crystallographic axes and the angles at which they meet, while the systematic absence of certain diffracted beams gives information as to the space group of the crystal. The positions of the atoms within the unit cell can only be determined by measurement of the intensities of the diffracted beams; the ideal method would be to measure these intensities and then combine them by calculation to form an image of the structure. As is well known this cannot be done without a knowledge of the relative phases of the diffracted beams and there is no way of determining these by direct experiment.

Mathematically expressed,

$$\rho(xyz) = \frac{1}{V} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} F(hkl) \cos(2\pi hx + 2\pi ky + 2\pi lz - \alpha)$$

$\rho(xyz)$ is the electron density at the point (xyz)

$F(hkl)$ is the ratio of the amplitude of the wave scattered by all the atoms in the unit cell, in the given direction, to that scattered by a single electron under corresponding conditions. F is usually called the structure amplitude.

α is the phase of the wave relative to that diffracted in the same direction by an electron situated at the origin of the unit cell. The fact that α is in general unknown constitutes the fundamental difficulty of X-ray analysis.

If the crystal possesses a centre of symmetry the phase angles are all zero or 180° and we may write

$$\rho = \frac{1}{V} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} F(hkl) \cos 2\pi(hx + ky + lz)$$

where F may be either positive or negative.

The corresponding result for the electron density projected on (001) is

$$\rho(xy) = \frac{1}{A} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} F(hko) \cos 2\pi(hx + ky)$$

this equation holds when the plane group symmetry of the projection includes a centre of symmetry.

Again F may be either positive or negative and in general it is not possible to decide which alternative is correct.

These difficulties can be overcome in certain cases.

METHOD 1.

If the structure is a simple one the probable arrangement of the atoms may be guessed at and the correctness of the assumption tested by comparing calculated and observed structure amplitudes. When satisfactory agreement has been obtained the Fourier series method may be used to refine this structure, α or the sign of F being obtained by calculation from the approximate structure. The method is essentially one of trial and error and is applicable only in the final stages of the determination of complex organic structures.

METHOD 2.

If an atom is present whose diffracting power (atomic scattering factor) is much greater than that of any other atom in the structure, and these other atoms are few in number, then the wave scattered by this atom exerts an over-riding effect and approximately correct values of α may be calculated from a knowledge of the position of this single atom. This method could be applied to certain sugar derivatives containing a bromine or iodine atom.

METHOD 3.

If one atom of the crystalline compound A can be replaced by another of different atomic number so as to give a crystalline compound B isomorphous with A, and if the space group symmetry

of the crystals includes a centre of symmetry then from a knowledge of the coordinates of the replaceable atom and the magnitude of the structure amplitudes $F_A(hkl)$ and $F_B(hkl)$ the signs of the F 's may be deduced.

When the space group symmetry does not include a centre of symmetry but the plane group of the projection on (001) does, the signs of $F_A(hko)$ and $F_B(hko)$ may be found.

Three or two-dimensional Fourier synthesis can then be carried out.

This is one of the most powerful methods available for the determination of complex crystal structures, and has been successfully used by Cox and Jeffrey ⁽²⁾ to determine the structure of glucosamine hydrobromide. The fact that two isomorphous compounds must be available means that the method is of limited application.

METHOD 4.

The Patterson function⁽⁴⁾

$$P(uvw) = \frac{1}{V^2} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} F^2(hkl) \cos 2\pi(hu + kv + lw)$$

exhibits maxima at vector distances from the origin equal to vector distances between pairs of maxima in the electron density, i.e. between pairs of atoms.

The Patterson function does not involve the phase angle α . Harker has pointed out⁽⁵⁾ that the Patterson

function over a particular plane or along a particular line may give information concerning vectors between atoms related by a symmetry element of the space group and that special value attaches to vectors of this type, since their coordinates are directly related to the atomic coordinates. This method is applicable to all but triclinic crystals. The Patterson and Patterson-Harker methods become involved when applied to structures with large numbers of atoms such as organic structures in general, owing to the excessively large number of interatomic vectors. Nevertheless in studying complex structures the normal procedure nowadays is to carry out an F^2 synthesis to see if it yields any clear information on the general form or orientation of the molecules.

CHAPTER 1.PATTERSON-HARKER METHOD APPLIED TO SUCROSE.

Sucrose crystallises from aqueous solution in the form of clear anhydrous crystals which may attain several cms. in dimensions if allowed to grow slowly.

Groth, Chemische Krystallographie 3, 448, gives the following information:

Monoclinic sphenoidal, $a:b:c = 1.2595: 1: 0.8782$

$$\beta = 103^{\circ}30'$$

Becker and Rose found (6)

$$a = 10.65, b = 8.70, c = 8.00 \text{ \AA.} \quad \therefore a:b:c = 1.225: 1: 0.92$$

$$\beta = 105.74^{\circ}, \text{ Space group } P2_1, d = 1.574 \text{ for } Z = 2$$

Beevers and Robertson found (unpublished)

$$a = 10.70, b = 8.69, c = 7.72 \text{ \AA.} \quad \therefore a:b:c = 1.231: 1: 0.889$$

$$\text{Space group } P2_1, d = 1.582 \text{ for } Z = 2$$

The latter results are in better agreement with those of Groth and with the observed density of 1.595 gm/cc.

The symmetry element of $P2_1$ consists of a two-fold screw axis through the origin. The equivalent points are

$$(x, y, z) \text{ and } (\bar{x}, y + \frac{1}{2}, \bar{z})$$

Suppose the unit cell to contain a single atom at the point (x, y, z) together with that at the equivalent point $(\bar{x}, y + \frac{1}{2}, \bar{z})$

The vectors between these atoms can be represented by lines from the origin to the points

$$(2x, \frac{1}{2}, 2z) \text{ and } (\bar{2}x, \frac{1}{2}, \bar{2}z)$$

The vector from the origin to the point $(2x, \frac{1}{2}, 2z)$ will be referred to simply as the vector at $(2x, \frac{1}{2}, 2z)$

The Patterson function therefore has maxima at the origin and at the points

$$u = 2x, v = \frac{1}{2}, w = 2z \text{ and } u = \bar{2}x, v = \frac{1}{2}, w = \bar{2}z$$

Thus by evaluating the function

$$P(u\frac{1}{2}w) = \frac{1}{V^2} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} F^2(hkl) \cos 2\pi(hu + k/2 + lw)$$

the x and z co-ordinates of the atom could be obtained. $P(u\frac{1}{2}w)$ is the Patterson-Harker function and the map of this function will be called the Patterson-Harker diagram. When the unit cell contains several atoms each atom at the point $(x y z)$ is represented by a peak on the Patterson-Harker diagram at $u = 2x, w = 2z$.

It thus appears that the Patterson-Harker diagram, when reduced in scale by a factor of two, has peaks at the points occupied by atoms in a projection of the structure on (010) . That certain

peaks may occur which do not represent atomic positions may be shown in the following way:

Consider two atoms at the points

$$(x_1 \ y_1 \ z_1) \text{ and } (x_2 \ y_2 \ z_2)$$

together with those at the equivalent points

$$(\bar{x}_1 \ y_1 + \frac{1}{2} \bar{z}_1) \text{ and } (\bar{x}_2 \ y_2 + \frac{1}{2} \bar{z}_2)$$

These four atoms give rise to sixteen interatomic vectors of which four coincide at the origin. The remaining twelve may be derived from the six listed below by the operation of a centre of symmetry at the origin. These six are given by:

	u.	v	w
(1)	$x_1 - x_2$	$y_1 - y_2$	$z_1 - z_2$
(2)	$x_1 - x_2$	$y_2 - y_1$	$z_1 - z_2$
(3)	$x_1 + x_2$	$y_1 - y_2 + \frac{1}{2}$	$z_1 + z_2$
(4)	$x_1 + x_2$	$y_2 - y_1 + \frac{1}{2}$	$z_1 + z_2$
(5)	$2x_1$	$\frac{1}{2}$	$2z_1$
(6)	$2x_2$	$\frac{1}{2}$	$2z_2$

(1) and (2) together with (3) and (4) are related by the operation of a mirror plane at $v = 0$.

(5) and (6) are in special positions with respect to this mirror plane, and in general they are the only vectors represented on the Patterson-Harker diagram. However if $y_1 - y_2 = \frac{1}{2}$ there is a peak of double weight

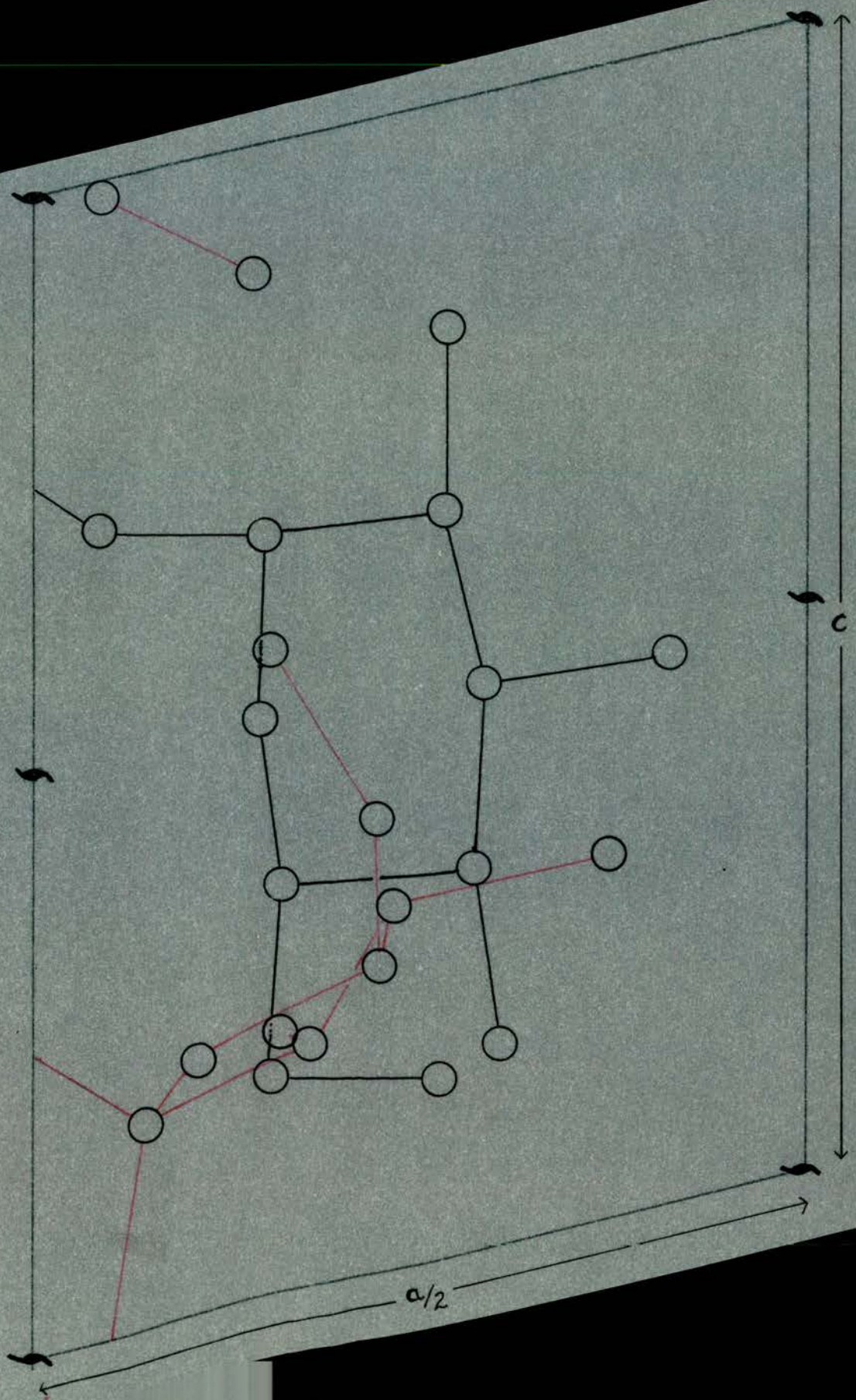
at $(x_1 - x_2, z_1 - z_2)$ and if $y_1 - y_2 = 0$ there is one of double weight at $(x_1 + x_2, z_1 + z_2)$ on this diagram. These peaks of double weight may be called "chance" peaks, since they represent vectors between atoms belonging to the same molecule which happen to have a particular separation in the direction of the b-axis. Those of the type $(x_1 + x_2, z_1 + z_2)$ occur midway between two of the type $(2x, 2z)$. It may be noted that a chance peak at $(x_1 - x_2, \frac{1}{2}, z_1 - z_2)$ is always accompanied by one at $(x_1 + x_2, 0, z_1 + z_2)$ while one at $(x_1 + x_2, \frac{1}{2}, z_1 + z_2)$ is accompanied by one at $(x_1 - x_2, 0, z_1 - z_2)$. The number of peaks of the Patterson-Harker diagram which do not represent atomic positions is thus equal to the number of maxima exhibited by the Patterson function taken over the plane $v = 0$.

The presence of peaks which do not represent atomic positions is a complication, but it is a minor one compared with another which is insufficiently stressed in the literature. (Bunn makes no mention of it in discussing the Patterson-Harker method, Chemical Crystallography, p. 357) This is that while the Patterson-Harker diagram, reduced in scale by a factor of two, represents the structure projected on the basal plane of the unit cell, the Patterson-Harker diagram on its original scale has the same repeat-

distances a and c as the unit cell. Thus a structure whose projection is completely contained within the outline of the unit cell can only be contained within the outline of four identical contiguous Patterson-Harker diagrams. But the outline of these four contiguous diagrams contains the projections of eight molecules related to one another by the centres of symmetry possessed by each of the four components, while the outline of the cell takes in only the two molecules contained therein.

What this means in practice can best be illustrated by an example. Fig. 3.1 represents one possible appearance of the sucrose structure projected on (010). The unique area of the projection is shown, and contains the glucose residue (bonds in black) with the fructose residue in the other half of the unit cell. The operation of the screw axis causes this part of the molecule also to appear in the unique area of the projection, it is shown with bonds in red. This postulated structure is not of course the correct one and is reproduced simply to show the complexity of the Patterson-Harker diagram corresponding to a given structure. The corresponding area of the Patterson-Harker diagram is shown in Fig. 3.2 on the same scale. The unique area is included within the red lines. This

figure shows how much the situation is complicated by the introduction of additional centres of symmetry. The existence of only two chance peaks has been assumed. Those peaks which correspond to the atomic positions of Fig. 3.1 can be distinguished since the diagrams have been arranged to fit one over the other.



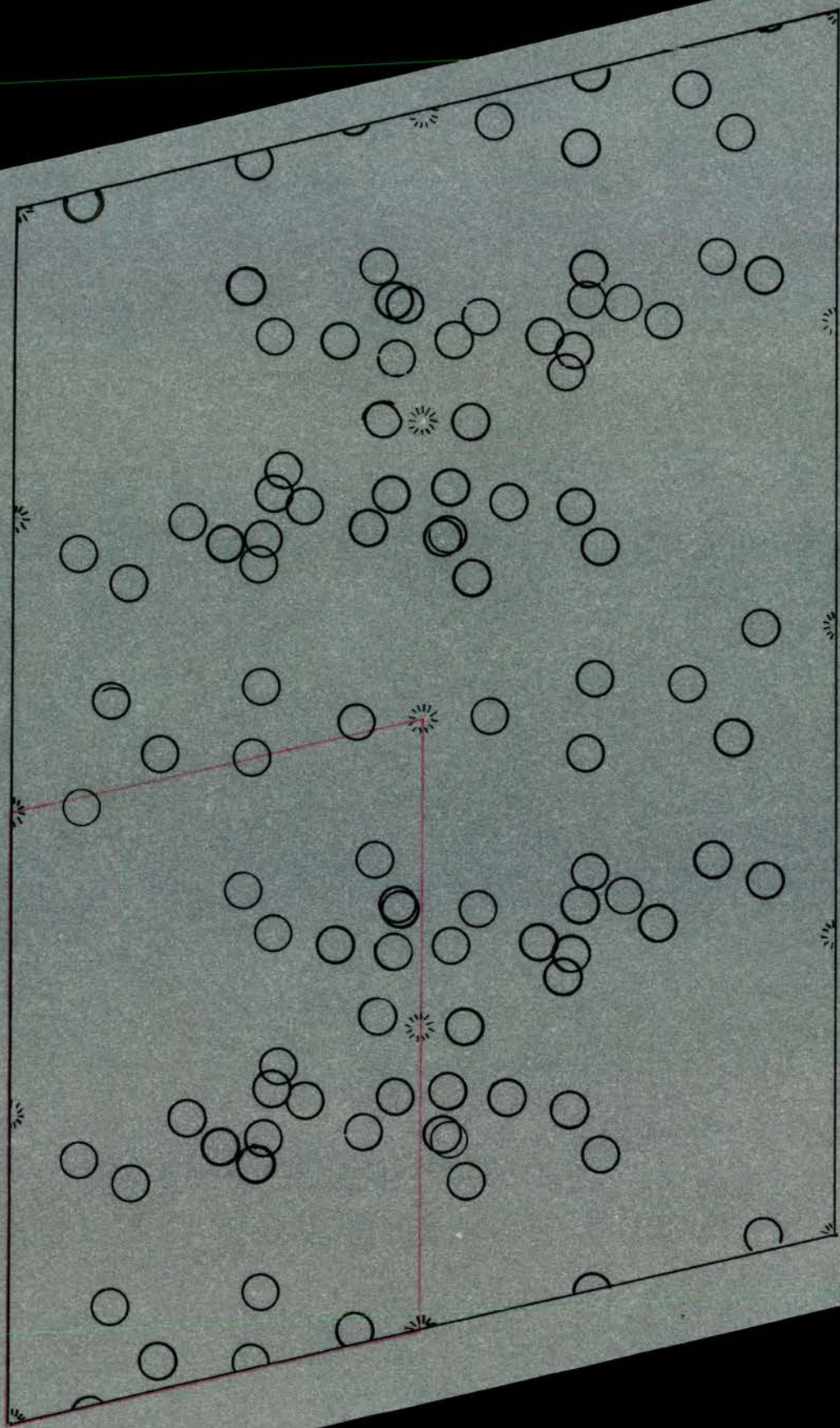


Fig. 3.1 (upper) & 3.2 (lower).

It should be borne in mind that in practice the peaks of the Patterson-Harker diagram are rather diffuse so that two whose centres lie within about $\frac{1}{2}$ A. from one another are not separately resolved, and that the diagram is derived from observed values of F^2 which are subject to experimental error.

Nevertheless this is the only direct way of investigating the sucrose structure by X-rays, and it was felt that since the sucrose molecule possesses two distinctive features - a ring of six atoms and another of five, these might possibly show up in the Patterson-Harker diagram.

Accordingly almost all the reflections from sucrose obtainable with $\text{CuK}\alpha$ radiation were photographed by the Weissenberg method and intensities estimated by visual comparison with a photographic wedge.

Relative values of F^2 obtained in this way were combined in a two-dimensional Fourier synthesis to give the function $P(u \frac{1}{2} w)$, and this function was drawn out on a scale of $1'' = 1 \text{ A.}$, contours being drawn in the usual way to form a Patterson-Harker diagram.

Models of the pyranose and furanose rings (on a scale of $2'' = 1 \text{ A.}$), as they were expected to occur in sucrose, were made from small spheres connected by steel rods, these were projected on the diagram in various ways by having a lamp at a distance of a few

yards cast a shadow of the model on the diagram. But even after the completion of other work described in this thesis, when the conformation of the pyranose and furanose rings was known with some certainty, it was not found possible to interpret the results in this way, so that the difficulties discussed above have so far proved insuperable in this case. In particular the function $P(u \text{ o } w)$ shows about twenty maxima, therefore about twenty of the peaks of the Patterson-Harker diagram do not correspond to atomic positions.

Most of this work was carried out by Beevers and Robertson and has therefore been described very briefly.

The writer tried to develop this method a stage further by evaluating the Patterson function at levels other than $v = \frac{1}{2}$ in order to find if information could be derived from the positions of vectors of the type $(x_1 - x_2, y_1 - y_2, z_1 - z_2)$ and $(x_1 + x_2, y_1 - y_2 + \frac{1}{2}, z_1 + z_2)$. The computations involved occupied several weeks, and the results obtained could not be interpreted. This method was therefore abandoned.

CHAPTER 2.

COMPOUNDS OF SUCROSE.

The failure of the direct method described in Chapter 1, caused attention to be transferred to certain crystalline compounds of sucrose. Derivatives of sucrose are comparatively few in number, and those difficulties which caused the investigation of sucrose itself to be unsuccessful would be equally operative in an investigation of most of its derivatives; there is the added objection that the process of say, methylation, may be accompanied by changes in the ring structure. It is therefore very fortunate in this connection that sucrose forms addition compounds with certain inorganic salts - notably the halides of the alkali metals - in which the sucrose molecule appears to act as a single unit. The existence of a number of such compounds has been reported, but no suggestion as to their nature has been made in the literature. It may safely be assumed, however, that in such compounds sucrose preserves its internal structure unchanged, except possibly for a change in the relative orientation of the fructose and glucose residues due to rotation about the bonds which join them to their common

oxygen atom. The investigation of a crystalline compound of this type is thus potentially capable of yielding all the information which would be obtained by a successful investigation of sucrose itself, at least as regards the structure of the molecule. Against the objection that it would not give information regarding the crystal structure of sucrose may be set the possibility that it would give information not only as to the forces between hydroxyl groups but also as to those which must exist between hydroxyl groups and ions in a structure of this kind. This might help to throw light on the nature of organic-inorganic complexes such as have been studied by MacEwan⁽⁷⁾ and Bradley⁽⁸⁾. These addition compounds therefore merit investigation apart from the fact that sucrose is a constituent.

The published work on the subject mainly dates from the previous century and conflicting evidence is presented on several points. The method of examination appears to have consisted almost entirely of chemical analysis, in a few instances only do the crystals appear to have been examined optically or crystallographically. Probably, therefore, some of the "compounds" were close mixtures of the constituents in proportions which by chance agreed with a particular formula. A critical examination of the

literature led to the conclusion that the existence of the following crystalline compounds had been definitely established. (Suc. = $C_{12}H_{22}O_{11}$)

(1) Suc. Na Cl. $2H_2O$ was obtained by Maumené⁽⁹⁾ in the form of large colourless orthorhombic crystals of density 1.574 gm/cc. This substance was also prepared by Gill⁽¹⁰⁾. Other investigators have mentioned that they were unable to obtain it.

(2) Suc. Na Br. $1\frac{1}{2}$ (?) H_2O was obtained by Gill⁽¹⁰⁾ in the form of small white needles.

(3) Suc. KCl. $2H_2O$ was prepared by Mackenzie and Quinn⁽¹¹⁾ by mixing solutions of sucrose (1 mol.) and KCl (1 mol.) in the minimum quantities of boiling water. The crystals were deposited on cooling over sulphuric acid.

(4) 2 Suc. 3 Na I. $3H_2O$ was prepared by Gill (loc. cit.) who states that it crystallises from a solution in water of sucrose and sodium iodide in almost any proportions. Results of optical and goniometric measurements are given and are reproduced in Groth, Chem. Kryst. 3, 448. The crystals are monoclinic and have a density of 1.854 gm/cc.

Gautier⁽¹²⁾ claims to have prepared practically all substances of the type Suc. AX. $2H_2O$, where A denotes an alkali metal and X a halide. Doubt is cast on the reliability of the results by his statement that the substance to which he ascribes the formula

Suc. Na I. $2\text{H}_2\text{O}$ was identical in appearance with that described by Gill, the correct formula for which is undoubtedly $2 \text{ Suc. } 3 \text{ Na I. } 3 \text{ H}_2\text{O}$. Other compounds containing CaO and BaO have been prepared, but do not appear to have been obtained in crystalline form.

Those compounds which seem most likely to repay X-ray investigation are $2 \text{ Suc. } 3 \text{ Na I. } 3\text{H}_2\text{O}$, to which the "heavy-atom" method could be applied, and the series of compounds formed with the halides of the alkali metals, which may be expected to be members of an isomorphous series.

INVESTIGATION OF SODIUM IODIDE SUCRATE.

An aqueous solution of two molecular proportions of sucrose to three of sodium iodide was kept at an estimated temperature of 40°C . and in a few days a somewhat irregular mass of crystals was deposited. A few of the smaller crystals were used to seed a similar solution which was allowed to evaporate more slowly. Large regular crystals were obtained in this way. Chemical analysis and examination on the optical goniometer showed these to be identical in chemical composition and crystallographic form with those described by Gill. A cylindrical specimen of diameter 1 mm. was cut from a large crystal in the direction of the b-axis and X-ray oscillation

and Weissenberg photographs taken. (Details of experimental procedure are given in a subsequent section in connection with a more detailed investigation of other substances). Measurements made on these photographs show

$$a = 29.4, b = 8.2, c = 8.50 \text{ \AA.}, \beta = 94.05^\circ$$

The space group has not been determined, but is no doubt $P2$ or $P2_1$, glide planes and mirror planes being ruled out by the presence of the asymmetric sucrose molecule of which only the d-form exists. Since the measured density of this substance is 1.854 gm/cc. the unit cell contains two of the complex molecules $2 \text{ Suc. } 3 \text{ Na I. } 3\text{H}_2\text{O.}$

It is therefore not suitable for complete X-ray investigation for the following reasons:

The fact that there are four molecules of sucrose, six of sodium iodide and six of water in a monoclinic unit cell means that in any projection of the structure down a crystal axis, such as is given by a two-dimensional Fourier synthesis, a considerable amount of molecular overlapping is inevitable.

The comparatively great length of the a -axis means that values of $F(h \ k \ l)$ up to about $h = 40$ would have to be measured if copper radiation was used. The amount of work involved in carrying out the computations necessary to obtain even a two-dimensional electron density map would be considerable, and the

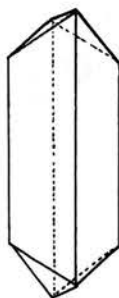
Beevers-Lipson strips used in such computations are only available for values of h less than 20.

These difficulties are not insuperable, but the investigation of this substance was not taken further in the hope that more promising material would be found.

Preliminary investigation of sodium bromide sucrate and sodium chloride sucrate.

That the hope expressed above was realised is due to the foresight of Mr. J.H. Robertson, who in September 1943 had made up a few solutions of sucrose with sodium bromide in varying proportions, also a few with sodium chloride. These solutions remained undisturbed in a corner of the laboratory for over fifteen months. It was noticed that crystals were growing from a solution containing two molecular proportions of sucrose to three of sodium bromide. They occurred as prisms which appeared to have grown from a common centre of crystallisation, a drawing (not accurately to scale) of one such prism is given below.

Fig. 4.1



The faces of the crystals were somewhat irregular and accurate goniometric measurements have not been made. The total mass of crystals deposited was about 2.5 gm.

A solution of 0.7340 gm. of the crystals in 25 ccs. of water rotated the plane of polarised light by 1.39° . $[\alpha]_D^{20} = 66.6$ gives the percentage of sugar present in the crystals as 71.1. Titration of this solution against N/10 silver nitrate showed that sodium bromide was present to the extent of 21.4%. When a small correction is made to allow for the fact that the presence of sodium bromide lowers the specific rotation of sucrose (von Lipmann, Chemie der Zuckerarten. p. 1191) the final figures are

Sucrose	NaBr	Water (by difference)	
71.3%	21.4%	7.3%	Measured.
71.1%	21.4%	7.5%	Calculated.

The calculated values are based on the formula $\text{Suc. NaBr} \cdot 2\text{H}_2\text{O}$, which is thereby shown to be correct.

Another solution which had been made up several months previously consisted of one molecular proportion of sucrose to two of sodium chloride. An irregular close-packed mass of crystals had formed, from these two small crystals of regular shape were picked out. Part of the larger mass of crystals was analysed by the method outlined above giving:

Sucrose	NaCl	Water (by difference)
77.5%	19.2%	3.3%

These results do not agree with the formula $\text{Suc. NaCl. } 2\text{H}_2\text{O}$ although they agree moderately well with a formula such as $2 \text{ Suc. } 3 \text{ NaCl. } (2 \text{ or } 3) \text{ H}_2\text{O}$. Later, after a preliminary investigation of $\text{Suc. NaBr. } 2\text{H}_2\text{O}$ had been made by X-ray methods, rotation photographs of the two small crystals of regular shape were taken and these photographs showed that the small crystals, at least, consisted of $\text{Suc. NaCl. } 2\text{H}_2\text{O}$ since they gave the same layer-line spacing of spots as was given by $\text{Suc. NaBr. } 2\text{H}_2\text{O}$. Weissenberg photographs showed a strong correlation between the intensities of corresponding reflections. It is probable, therefore, that the irregular mass of material which was analysed chemically, consisted of a close mixture of sugar, salt and $\text{Suc. NaCl. } 2\text{H}_2\text{O}$. It has since been found that crystals of the compound grow more readily from a solution containing two molecular proportions of sucrose to three of sodium chloride. Evaporation must take place very slowly, any attempt to hasten the process by raising the temperature or lowering the pressure causes an irregular mass of crystals, mainly sucrose, to be deposited.

Preliminary investigation having established the fact that these two compounds (and possibly others such as $\text{Suc. K Cl. } 2\text{H}_2\text{O}$) are members of an isomorphous series, a complete X-ray investigation of both substances was made.

CHAPTER 3.

EXPERIMENTAL.

Apparatus.

The X-rays were produced by a Metropolitan-Vickers X-ray unit, normally run at 60 K.V., 25 m.a.. Cu $K\alpha$ radiation was used throughout the investigation, the $K\beta$ radiation being absorbed by a nickel filter.

The films used were Ilford double-coated X-ray film and Kodak Industrex D film. Development and fixing were carried out as recommended by the makers.

The camera was a Weissenberg of radius 5 cm. and vertical traverse 13.3 cm. per 180° rotation. The camera can of course be held stationary for the taking of oscillation photographs.

Preparation of crystal specimens.

The shape of the crystals of Suc. NaBr. $2H_2O$ suggests that they are orthorhombic and that one crystallographic axis is in the direction of the length of the prism, while the other two lie along the diagonals of the prism cross-section. This assumption was found to be correct since the oscillation photograph of a specimen with its axis in one of these three directions always consisted of spots distributed on layer lines, and the length of

an axis calculated from the spacing of layer lines obtained with one specimen always agreed with the length calculated from Weissenberg photographs of another specimen. That axis which lies in the direction of the length of the prism has been called the c-axis, the a and b axes correspond to the long and short diagonals of cross-section.

Specimens for photography were prepared by chipping away parts from a single crystal with a razor-blade until a roughly cylindrical portion remained, the length of the cylinder being approximately in the direction of an axis. The cylinder was then smoothed by rolling it between two pieces of fine sandpaper until its diameter was 1.1 mm. With a little practice specimens can be prepared whose diameter does not vary by more than 0.1 mm. and whose axis is within 5° of the crystallographic axis. The specimen was then attached to a glass rod by means of durofix and mounted on the goniometer. The crystal cylinder was adjusted to lie on the axis of rotation of the instrument by rotating the goniometer with the crystal in the field of view of a microscope fitted with an eyepiece scale.

Orientation of specimen.

Since each specimen was cylindrical in shape no crystal faces remained which could be used to orient it by optical methods. A simplification of the method of Hendershot⁽¹³⁾ was used.

Suppose the crystal axis makes an angle ϕ with the axis of the camera in the vertical plane which contains the X-ray beam and an angle ψ in a perpendicular vertical plane. By considering the intersection of the zero layer of the reciprocal lattice network with the sphere of reflection we find that if the displacement is wholly in the plane containing the X-ray beam, i.e. $\psi = 0$ when the goniometer is in the centre of its range of oscillation then the zero layer line spots of a photograph taken with the specimen oscillating through a small angle (10°) lie on a curve of the form shown in Fig. 5.1. If y is the displacement of this curve from the equatorial line at a point which corresponds to $2\theta = 90^\circ$, reference to Figs. 5.2 and 5.3 shows that $y = \phi r$, where r is the radius of the camera (5 cms.)

If the displacement of the crystallographic axis from the camera axis is wholly perpendicular to the vertical plane containing the X-ray beam, i.e. $\phi = 0$ when the crystal is in the centre of its range of oscillation, the zero layer line spots lie on the curve shown in Fig. 5.4, and the maximum displacement of this curve from the equatorial line occurs when

$2\theta = 90^\circ$ and is given by $y^1 = \psi r$, as is shown by Fig. 5.5.

If both ϕ and ψ are finite the curve is of the form shown in Fig. 5.6 and clearly

$$y_1 = r\phi + r\psi, \quad y_2 = r\phi - r\psi$$

$$\therefore \phi = \frac{y_1 + y_2}{2r} \text{ and } \psi = \frac{y_1 - y_2}{2r}$$

The use of these two equations should enable the orientation to be corrected after a single oscillation photograph has been taken. In practice at least two such photographs must be taken. The first is taken with the camera screen removed so that several layer lines are recorded. y_1 and y_2 cannot be measured accurately from this photograph since the position of the equatorial line is rather uncertain. An adjustment can be made, however, which is sufficiently accurate to ensure that all the zero layer-line reflections will pass through a slit of width 1 cm. in the camera screen and be recorded on the second photograph. An accurate adjustment can be made using values of y_1 and y_2 taken from this photograph since the shadows of the slit edges form convenient reference lines. A final check is got by photographing the zero layer line through a slit of width 3.5 mm.

Fig. 5.1

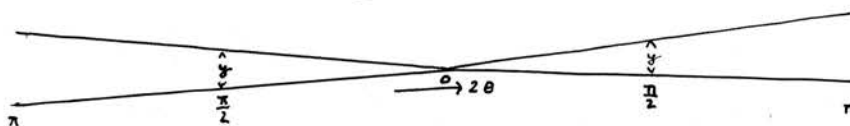


Fig. 5.2

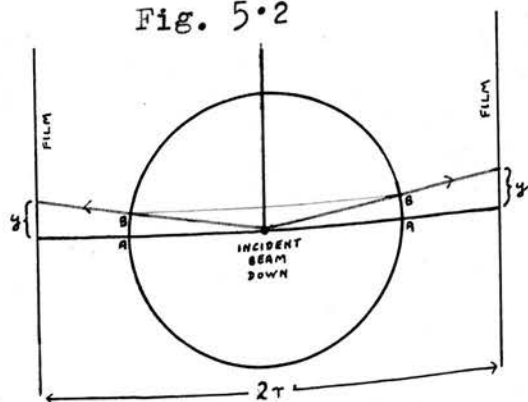
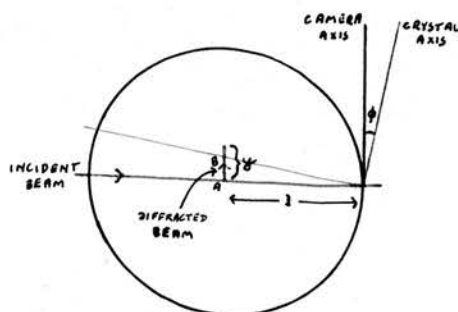


Fig. 5.3



From Fig. 5.3, $AB = \phi$, and from 5.2 $y/AB = r$
 ie. $y = \phi r$

Fig. 5.4

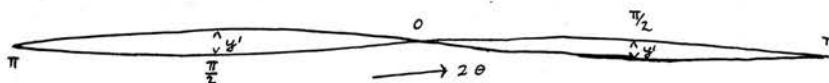


Fig. 5.5

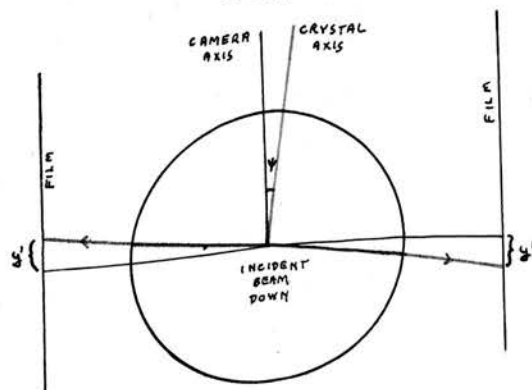
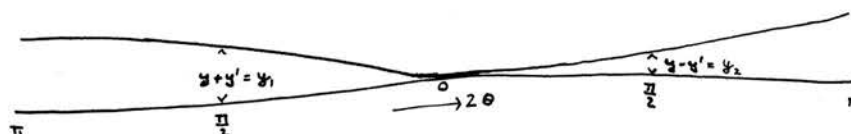


Fig. 5.6



Weissenberg Photographs.

Weissenberg photographs of individual layer lines can now be taken, the crystal being oscillated through an angle of 240° . About twelve such layer lines result from an a-axis specimen, these were photographed individually as far as the ninth. Four layer lines were photographed from each of the b and c-axis specimens. Three photographs of exposure times 6 h., 2 h., and $\frac{1}{2}$ h. were taken of each, in the case of zero layer line photographs the long exposure time was increased to 10 hours. The complete investigation of the two compounds thus involved the preparation and orienting of six crystal specimens and the taking of over one hundred Weissenberg photographs. In the early stages of this work it was found that the apparatus could not be left unattended for long because the current through the tube gradually increased; tube currents greater than 25 m.a. cause the target to puncture if continued for some time. A relay was therefore fitted which operated at 25 m.a., starting an electric motor which altered the tapping point of a variable resistance so as to decrease the filament current.

The following table summarises the results obtained by measurements on these photographs and in other ways.

	Suc. NaBr. $2H_2O$	Suc. NaCl. $2H_2O$
a	21.92 A.	21.75 A.
b	9.72 "	9.62 "
c	8.43 "	8.40 "
V	1796 A ³	1758 A ³
d(calc.)	1.778 gm/cc	1.651 gm/cc
d (obs.)	1.783 "	1.650 "
μ	43.4 cm ⁻¹	29.4 cm ⁻¹
Space group	P2 ₁ 2 ₁ 2 ₁	P 2 ₁ 2 ₁ 2 ₁

The unit cell dimensions were calculated from the positions of reflections of the type (h o o) etc. by the method of Bradley and Jay⁽¹⁴⁾. An example is given below.

h	θ	a	$\cos^2\theta$
28	79°32'	21.89 A.	0.033
26	66°11'	21.85	0.163
24	57°57'	21.77	0.282
22	51°08'	21.72	0.394
20	45°16'	21.64	0.496

Extrapolation to $\cos^2\theta = 0$ gives a = 21.92 A.

Densities were calculated from the formula

$$d = \frac{1.66 \text{ MZ}}{V}$$
 where M is the molecular weight, Z the number of Molecules in the unit cell (taken as 4) and V the volume of the unit cell in A³.

Densities were found experimentally by adding alcohol to bromoform until a small crystal remained suspended in the mixture. The weight of 10 ccs. of this liquid was then found. The measurements were made at 18°C and are probably accurate to within 0.005 gm /cc.

Absorption co-efficients were calculated from the formula $\mu = d \sum p. \mu/p$ where d is the density of the substance and p the proportion by weight of a constituent element of mass absorption co-efficient μ/p .

These are of interest since Buerger has shown (X-ray Crystallography p. 180) that the optimum diameter of a cylindrical specimen for photography is $2/\mu$. This works out at 0.46 mm and 0.70 mm in the case of the two substances in question, rather less than the value used, which was 1.1 mm for both.

The space group was deduced from the systematic absences

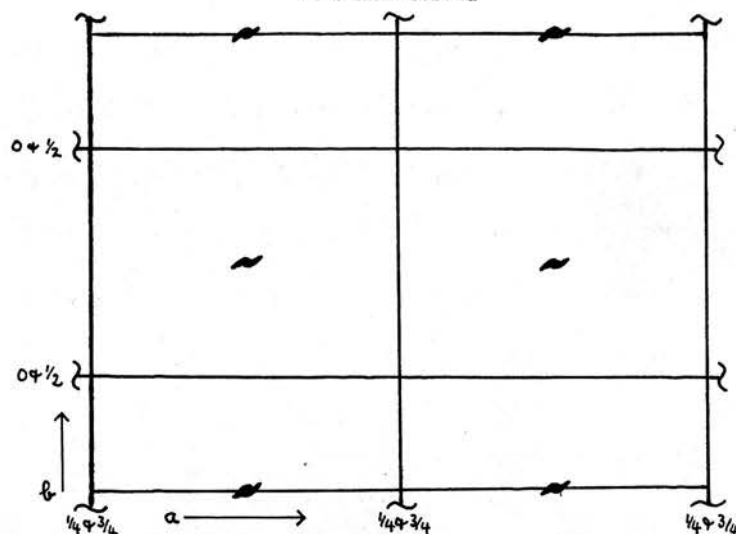
(hoo) when h is odd.

(oko) when k is odd.

(ool) when l is odd.

and there are no other systematic absences.

The symmetry elements of this space group are shown in Fig. 6.1.

FIG. 6.1.Indexing, and Assignment of Intensities.

So far this has been done for zero layer line reflections only. The indexing of spots on a Weissenberg photograph can be done almost completely by inspection, although a chart was found useful in indexing high orders. Intensity assignment has been done by a method which is more accurate than that generally employed. The customary method consists in the visual comparison of spots on the photograph with a wedge in the centre of the film, the steps of which have received amounts of X-ray energy proportional to the numbers 1, 2.....20 by exposing the different parts of the wedge to a uniform beam of X-rays for times in that ratio. (See, for instance, Hughes⁽¹⁵⁾, who estimates the accuracy of this method at $\pm 20\%$). This method was used in the early stages of this work, it suffers from the following disadvantages:

(I) The attention of the observer must constantly be transferred from the scale to other parts of the film. Comparison would be greatly facilitated if the scale could be held close to the spot being examined.

(II) The scale consists of twenty steps, each of uniform photographic density, while the spots vary in photographic density across their breadth because of absorption of the diffracted beam in the crystal. Efficient visual comparison of uniform and non-uniform photographic densities is difficult.

(III) The spots are viewed against a background of lower photographic density, caused by non-coherent scattering of X-rays by the crystal and the air inside the camera. The scale, on the other hand, is imprinted on a part of the film which has not been exposed to this radiation. Thus, for accuracy, two observations should be made, one of the intensity of the spot and one of the background intensity in its immediate neighbourhood, the latter should then be subtracted from the former. This correction is by no means negligible since the background intensity is of the same order of magnitude as that of the weaker reflections.

In attempting to estimate intensities by this method it was noticed that it was much easier to judge the departure from equality of the densities

of two spots than it was to compare either of them with the photographic wedge in the centre of the film. This observation forms the basis of the method finally adopted.

10^0 oscillation photographs of a specimen of sodium bromide sucrose were taken, the camera screen being arranged so that only reflections belonging to the zero layer line were recorded. Preliminary photographs showed that an exposure of 20 mins. was sufficient to cause a particular reflection to produce a spot having, at its maximum, about the limit of useful photographic density. This limit is due to the fact that photographic density increases very slowly with the amount of X-radiation received after a certain stage. Beyond this stage all amounts of X-ray energy are represented by almost the same photographic densities. It was also found that with an exposure of 1 min. the resulting spot was just detectable. Photographs of this reflection were taken of exposure times, 20, 18, 16, 14, 12, 10, 8, 7, 6.....1 min. (Actually the last few were taken by keeping the time of exposure constant and reducing the current through the tube in the required ratio, otherwise the time of exposure would have become comparable with the period of oscillation of the specimen). These fourteen photographs were taken on the same film, the camera being moved through a distance of 1

cm. between each. Hence finally fourteen spots were obtained whose photographic densities corresponded to X-ray intensities in a known ratio. Intensities could now be estimated by moving this scale beside the spot under examination until one was found which appeared identical when viewed by diffusely transmitted light. This method eliminates some of the objections listed above:

- (I) The scale is held close to the spot being examined.
- (II) The variation in photographic density across the breadth of the spot under examination and across that on the scale is the same if the former has approximately the same Bragg angle as the latter (about 25°).

This is not so for spots of Bragg angle greater than about 35° , an intensity was given to the latter which corresponded to their maximum photographic density.

- (III) No correction for the effect of the background is necessary because the scale is viewed through the same background as the spot being examined. The accuracy of this method can be assessed from the following table, which gives the intensities assigned to reflections (hoo) of sodium chloride sucrate which are given by both b and c-axis specimens. The intensities listed in Rows (1) and (2) are thus quite independent, being taken from photographs of different crystal specimens.

h	2	4	6	8	10	12	14	16	18	20	22	24	26	28
(1)	0	224	144	220	224	3	6	42	0	30	0	2.5	5.5	30
(2)	0	220	150	255	250	4	8	44	0	31	0	2	5.5	31

Since the crystals are orthorhombic each spot appears four times on a Weissenberg photograph, twice on the L.H.S. and twice on the R.H.S. Intensities were assigned independently to each, an average of the four being taken. Systematic divergence between intensities assigned to spots on the L.H.S. and corresponding ones on the R.H.S. was found to be due to the fact that the X-ray beam was more intense on one side of the crystal than on the other, the collimating system was therefore adjusted to make the beam pass more exactly over the axis of rotation. Very occasionally systematic differences between the intensities of two identical reflections recorded on the same side of the film have been noticed, the reason for this is not known but the effect is too small to affect significantly the accuracy of the results.

Intensities were assigned to the weaker reflections by examination of the photograph of longest exposure time (10 h. for zero layer line photographs). Intensities greater than 20 (on the arbitrary scale used) were derived from the 2 h. or $\frac{1}{2}$ h. exposure photographs, and had therefore to be

multiplied by a factor inversely proportional to the relative exposure of the photograph from which they were derived. The apparent relative exposure of a photograph is only approximately proportional to the time of exposure because of variations in X-ray output, small inequalities in development conditions etc. and it was found that this factor could be estimated more accurately by comparing the intensities assigned to those reflections whose intensity fell within the range 1-20 on more than one photograph. For example, the average intensity of over 40 spots on a 10 h. photograph was 15.8, while the average intensity of the same spots on a 2 h. photograph was 3.0. All intensities derived from the 2 h. photograph must therefore be multiplied by the factor $15.8/3.0 = 5.27$ in order that they may be on the same scale as those taken from the 10 h. photograph. Intensities derived from photographs of an other specimen of the same substance were referred to this standard by comparison of intensities assigned to reflections of the type (hoo) etc. which are common to the zero layer line photographs of both specimens. (See, for example, the table on p. 43 where the ratio is almost unity, showing that intensities of the type (hko) are on the same scale as those of the type (hol)).

Correction for polarisation and Lorentz factors.

Zero layer sections of the reciprocal lattice were drawn on a scale 10 cm = 1., and the intensity $I(hk)$ of each reflection was written beside the corresponding lattice point (hk) . Each such lattice point is at a distance $2 \sin \theta$ from the reciprocal lattice origin. Values of the function $\Theta = (1 + \cos^2 2\theta)/\sin 2\theta$, at a suitable interval, were written out on a piece of transparent material, each value of Θ being written at a distance $20 \sin \theta$ cms. from a pin-hole near one end of the transparent scale. By pivoting this scale about a pin passed through the origin of the reciprocal lattice section the value of Θ corresponding to each lattice point, and therefore to each reflection, could be read directly from the transparent scale. (This method can be used to find rapidly for each possible reflection any factor which is a function of $\sin \theta$). The value of

$$10 I(hk)/\Theta = G^2(hk)$$

was written beside each reciprocal lattice point. The factor 10 was introduced to make the numbers $G(hk)$ of a convenient order of magnitude.

CHAPTER 4.

LOCATION OF BROMINE ATOM.

This was done by Patterson-Harker methods. It has already been mentioned that the Patterson function exhibits maxima at vector distances from the origin equal to vector distances between pairs of atoms.

$P(uv) = \frac{1}{R^2} \sum_{-\infty}^{+\infty} \sum F^2(hko) \cos 2\pi(hu + kv)$ represents this function projected on (001), its maxima give the components of the vectors in this plane. The equivalent points of $P 2_1 2_1 2_1$ are

α	β	γ	δ
(x, y, z)	$(x + \frac{1}{2}, \frac{1}{2} - y, \bar{z})$	$(\bar{x}, y + \frac{1}{2}, \frac{1}{2} - z)$	$(\frac{1}{2} - x, \bar{y}, z + \frac{1}{2})$

Vectors between these points have components in (001) given below:

u	v	Between points.
$\frac{1}{2}$	$\frac{1}{2} + 2y$	$\alpha\beta, \gamma\delta$
$\frac{1}{2}$	$\frac{1}{2} - 2y$	$\beta\alpha, \delta\gamma$
$2x$	$\frac{1}{2}$	$\alpha\gamma, \beta\delta$
$2\bar{x}$	$\frac{1}{2}$	$\gamma\alpha, \delta\beta$
$\frac{1}{2} + 2x$	$2y$	$\alpha\delta$
$\frac{1}{2} - 2x$	$2\bar{y}$	$\delta\alpha$
$\frac{1}{2} + 2x$	$2\bar{y}$	$\beta\gamma$
$\frac{1}{2} - 2x$	$2y$	$\gamma\beta$

Vectors of this type will occur for each atom in the unique volume of the unit cell, and $P(uv)$ will exhibit corresponding maxima. In particular the vectors $(\frac{1}{2}, \frac{1}{2} \pm 2y)$ and $(\pm 2x, \frac{1}{2})$ will be represented by maxima in the functions $P(\frac{1}{2}, v)$ and $P(u, \frac{1}{2})$ at $v = \frac{1}{2} \pm 2y$ and $u = \pm 2x$ respectively.

Maxima in the Patterson function due to vectors between bromine atoms will be much greater than those due to vectors between other atoms present in the structure. The height of a peak due to a bromine-bromine vector is proportional to the mean value of the square of the bromine atomic scattering factor over the range within which intensities have been observed. ($0 < \frac{\sin \theta}{\lambda} < 0.7$ when $\text{CuK}\alpha$ radiation is used). This again is roughly proportional to the square of the atomic number of bromine, so that the ratio of the height of a bromine-bromine peak to the height of that due to any other single atom is approximately $36^2 / 7^2 = 26.7$ being the average atomic number of the other atoms present. We may therefore expect the peaks due to bromine-bromine vectors to stand out against a general background formed by the superposition of a large number of smaller peaks.

Thus the function,

$$P(u, \frac{1}{2}) = \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} F^2(hko) \cos 2\pi(hu + k/2)$$

will have a large maximum at $u = \pm 2x$ and the function

$$P(\frac{1}{2}, v) = \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} F^2(hko) \cos 2\pi(h/2 + kv)$$

will have one at $v = \frac{1}{2} \pm 2y$

where x and y are co-ordinates of the bromine atom.

Due to the symmetry of the unit cell these functions reduce to (omitting proportionality constants):

$$P(u \frac{1}{2}) = \sum_{\substack{h=0 \\ \vdots \\ k}}^n \left\{ \sum_{\substack{k=0 \\ \vdots \\ h}}^n (-1)^k F^2(hko) \right\} \cos 2\pi hu$$

and

$$P(\frac{1}{2} v) = \sum_{\substack{h=0 \\ \vdots \\ k}}^n \left\{ \sum_{\substack{k=0 \\ \vdots \\ h}}^n (-1)^h F^2(hko) \right\} \cos 2\pi kv$$

In the same way line sections of the Patterson function projected on (010) and (100) will give the (xz) and (yz) co-ordinates of the bromine atom. Two independent values are thus obtained for each co-ordinate.

Values of F^2 in absolute units were not available at this stage of the investigation, values of G^2 (as defined on p.45) were used instead as co-efficients in the one-dimensional syntheses. This should have no effect on the position of the peaks, although it may change their shape.

The results obtained in this way are shown graphically in Graphs 1, 2 and 3. The functions exhibit large maxima as expected.

From Graph 1.

$$u = 2x = \pm 7.8/60, \quad x = 7.8/120 \text{ (choosing +ve sign)}$$

$$v = \frac{1}{2} - 2y = \pm 9/60, \quad y = 21/120$$

From Graph 2.

$$u = \frac{1}{2} - 2x = \pm 22.2/60, \quad x = 7.8/120.$$

$$w = 2z = \pm 6.4/60, \quad z = 6.4/120.$$

From Graph 3.

$$v = 2y = \pm 21.4/60, \quad y = 21.4/120$$

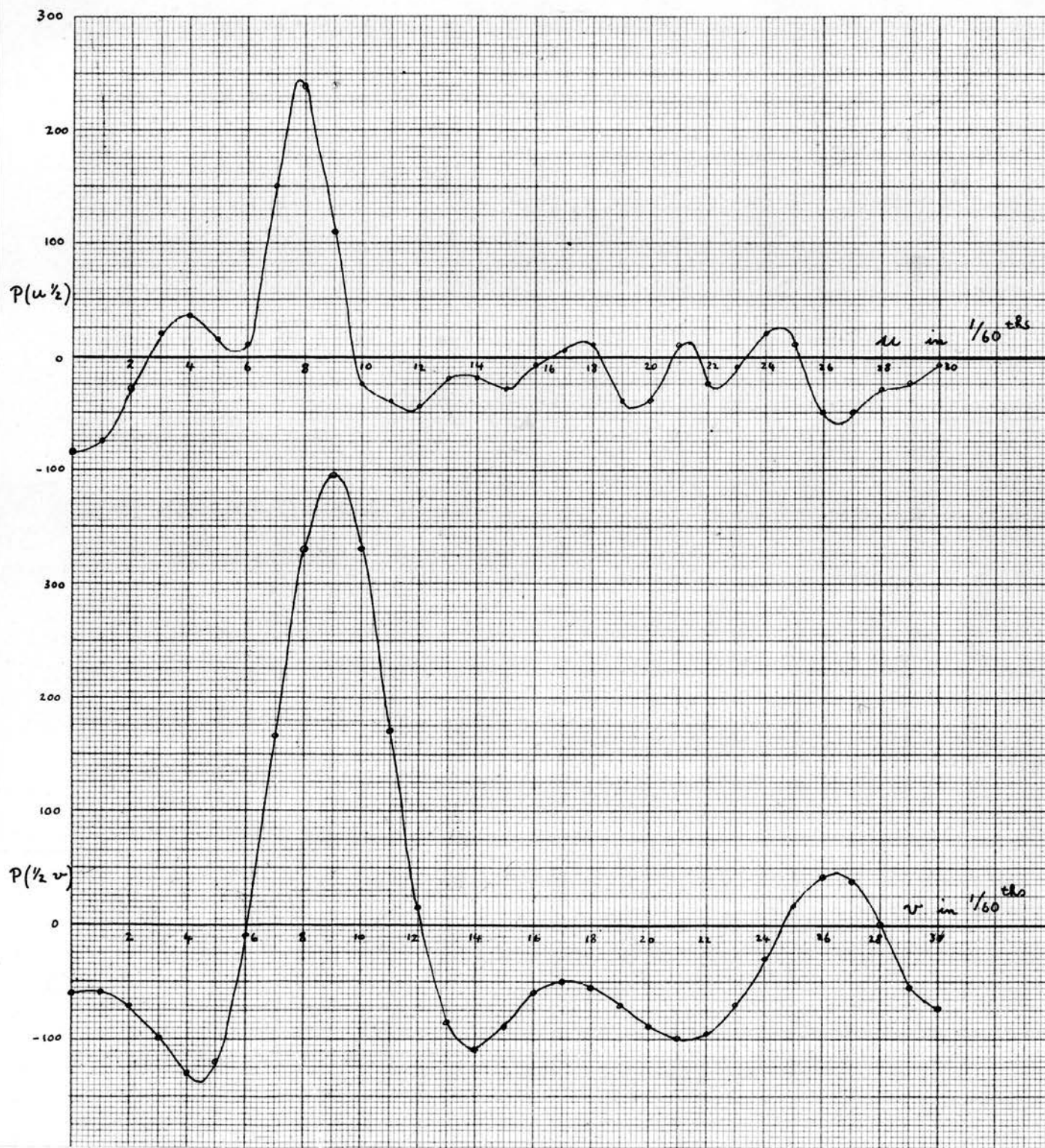
$$w = \frac{1}{2} - 2z = \pm 24.2/60, \quad z = 5.8/120$$

Taking average values, the bromine co-ordinates are therefore

$$x = .065, \quad y = .177, \quad z = .051$$

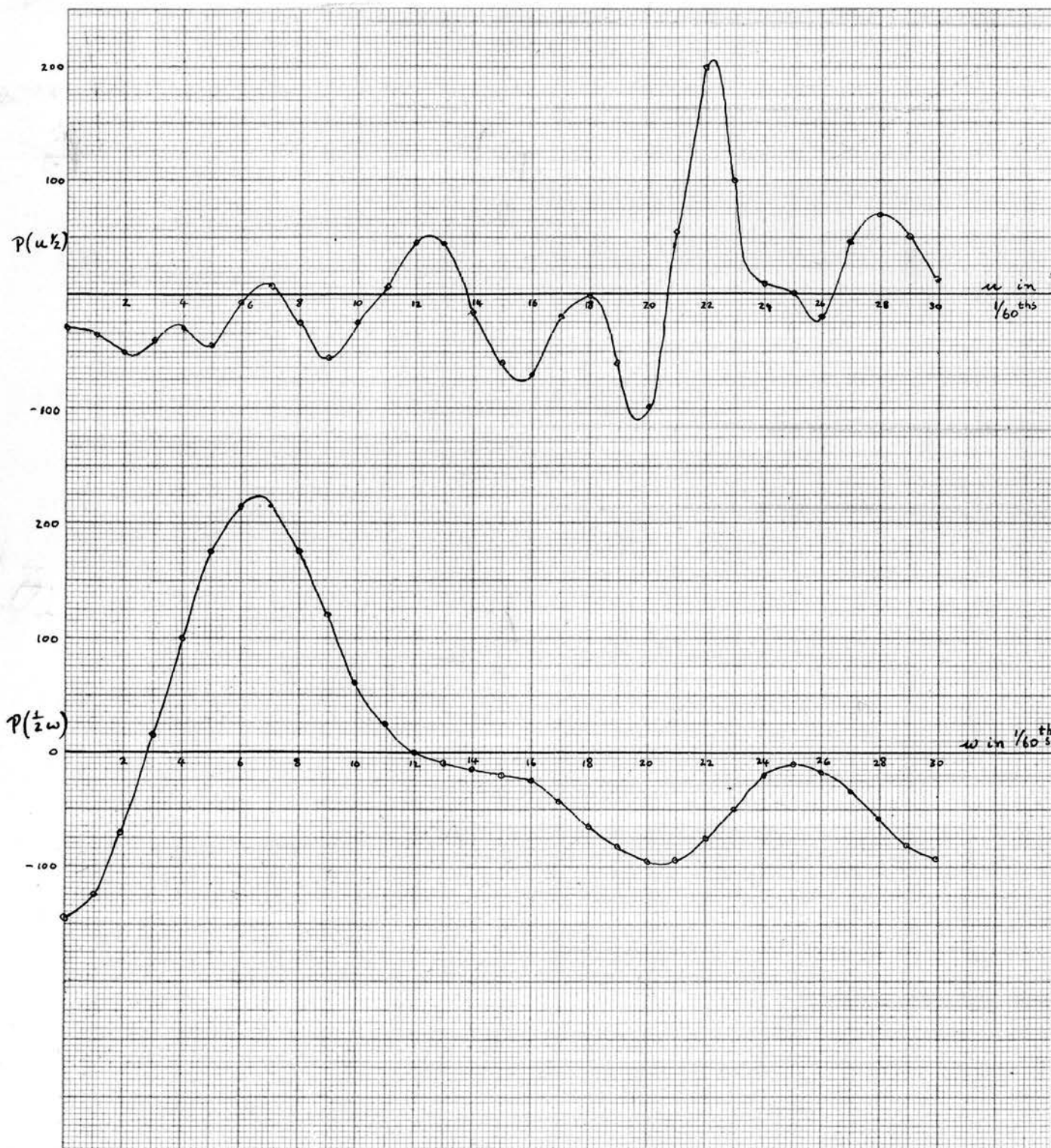
Graph 1.

Sections along the lines $v = \frac{1}{2}$ and $u = \frac{1}{2}$ of the
Patterson function projected on (001)



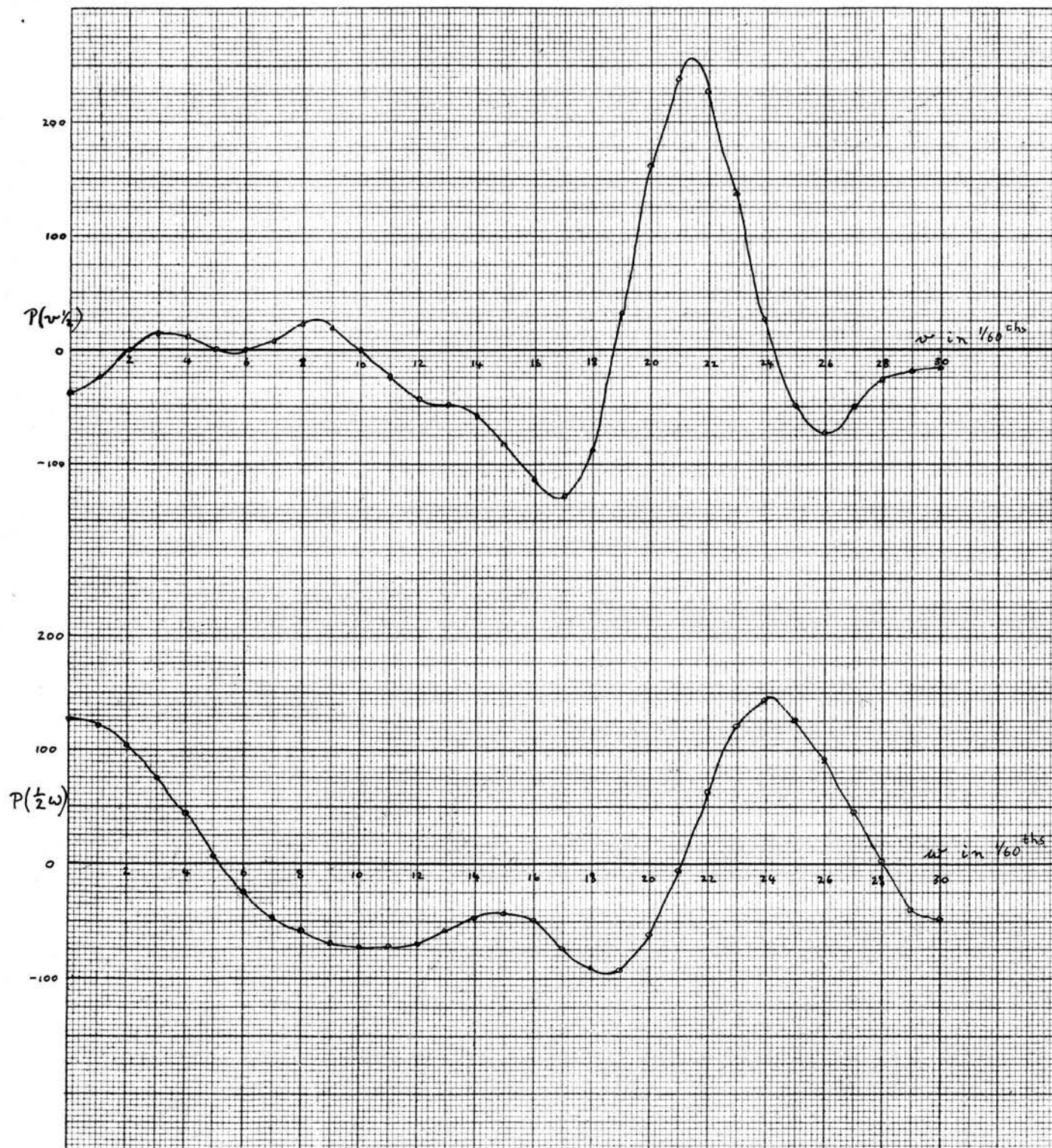
Graph 2.

Sections along the lines $w = \frac{1}{2}$ and $u = \frac{1}{2}$ of the Patterson function projected on (010).



Graph 3.

Sections along the lines $w = \frac{1}{2}$ and $v = \frac{1}{2}$ of the
Patterson function projected on (100)



CHAPTER 5.

ISOMORPHOUS REPLACEMENT METHOD.

The substances Suc. NaBr. $2H_2O$ and Suc. NaCl. $2H_2O$ are isomorphous, and the projection of their space group $P2_12_12_1$ down a crystallographic axis gives the plane group Pab which possesses centres of symmetry. Method 3 (of the introduction) can therefore be used to obtain maps of the electron density projected on (001), (010) and (100). The theory of this method will now be considered in more detail, taking the projection on (001) as example.

This projection possesses centres of symmetry at the points

$$(\frac{1}{4}, 0) \quad (\frac{3}{4}, 0) \quad (\frac{1}{4}, \frac{1}{2}) \quad (\frac{3}{4}, \frac{1}{2})$$

If the origin is transferred to the point $(\frac{1}{4}, 0)$ it will therefore coincide with a centre of symmetry.

The atomic structure factor referred to this origin is

$S(hk) = 4 \cos 2\pi hx \cos 2\pi ky$ when $h + k$ is even and $S(hk) = -4 \sin 2\pi hx \sin 2\pi ky$ when $h + k$ is odd.

Assuming that the atoms have the same co-ordinates in the crystal structures of Suc. NaBr. $2H_2O$ and Suc. NaCl. $2H_2O$ (denoted by subscripts B and C).

we may write:

$$F_B(hko) = Sf_B + \sum_i S_i f_i$$

$$\text{and } F_C(hko) = Sf_C + \sum_i S_i f_i$$

where f_B , f_C , f_i are atomic scattering factors, S is assumed the same for bromine and chlorine and subscript i denotes atoms other than bromine or chlorine.

$$\therefore F_B - F_C = S(f_B - f_C) \dots (1)$$

The R.H.S. of this equation involves quantities which are known or can be evaluated from the known position of the bromine atom. If $|F_B|$ and $|F_C|$ are known, the signs to be associated with each can be determined from this equation. It may be noted that $|F_B|$ and $|F_C|$ must be in absolute units.

Conversion of structure amplitudes to an absolute scale.

To explain how this was done it is necessary to make a digression in order to discuss the theory of the photographic method of intensity measurement in more detail than has been done in Chap. 3.

A crystal of volume V completely bathed in X-radiation gives the "integrated reflection"

$$P' = V \left(\frac{Ne^2 F(hko)}{mc^2} \right)^2 \cdot \lambda^3 \cdot \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} \cdot \exp. \left(\frac{-B \sin^2 \theta}{\lambda^2} \right) \cdot A(\mu r, \theta) \dots (2)$$

(Adapted from Bragg, the Crystalline State pp. 216-218)

The integrated reflection is defined by the equation:

$$P^I = \int_{\theta-\epsilon}^{\theta+\epsilon} \frac{R(\alpha) d\alpha}{P}$$

where $R(\alpha)$ is the amount of radiation reflected from the crystal per sec. when the normal to the plane (hko) makes an angle α with the incident beam and P is the amount of radiation incident on the crystal per sec. The integration is taken over a range 2ϵ (a few degrees) about the angle θ . P^I may be measured by means of the X-ray spectrometer, but it is difficult to measure in absolute units by the photographic method for two main reasons:

The intensity of the reflected beam is so extremely small compared with that of the primary beam that direct comparison by a photographic method is almost impossible.

The photographic method is not well adapted to the measurement of the integrated reflection because of the form of the relationship between X-ray intensity and photographic density.

Means have been found to overcome these difficulties, but the apparatus required is elaborate (e.g. double crystal method of Robertson⁽¹⁶⁾, α -ray photometer of Astbury⁽¹⁷⁾). The ultimate objective

is generally, of course, the measurement of F^2 so that when p^2 has been found the following factors of Equ. (2) must be considered.

$$V \frac{(Ne^2)^2}{(mc^2)^2} \frac{\lambda^3}{2} \quad \text{is a constant for a given substance and wavelength}$$

provided specimens of the same volume V are used.

$$\odot = \frac{1 + \cos^2 2\theta}{\sin 2\theta} \quad \text{is a geometrical factor;}$$

the correction of the intensities for this factor has already been described (p.45).

$$\text{Exp. } \left(\frac{-B \sin^2 \theta}{\lambda^2} \right) \quad \text{is the temperature factor,}$$

B being a constant whose value is unknown for all but a few substances. This is not of great importance since if a Fourier synthesis is carried out using values of $F \cdot \exp. \left(\frac{-B \sin^2 \theta}{2\lambda^2} \right)$ as co-

efficients instead of F 's the atomic positions are simply represented by more diffuse electron density maxima than would otherwise be the case.

$A(\mu r, \theta)$ is a correction factor which takes account of the absorption of the diffracted (zero layer line) beam in a cylindrical crystal specimen of radius r and linear co-efficient of absorption μ (18)
Its direct application to intensities derived by the photographic method is of doubtful validity since this method does not measure integrated reflection.

All of these factors are functions of

$\sin \theta$ (at least for zero layer line reflections). We may therefore group together the constant term, absorption factor and temperature factor, writing

$$p^2 = F^2 \odot \cdot \psi(\sin \theta)$$

Now the intensity $I(hk)$ assigned to each reflection depends on the maximum photographic density of the corresponding spot, we may therefore expect $I(hk)$ to be proportional to the maximum value of the function $R(\alpha)$. In any case we may write

$$p^2 = \int \frac{R(\alpha) d\alpha}{P} = I(hk) \cdot \phi(\sin \theta)$$

where ϕ is some (unknown) function of $\sin \theta$.

Hence finally

$$F^2 \odot \cdot \psi = I \cdot \phi$$

$$\text{or } F(hko) = G(hko) \cdot g(\sin \theta)$$

where I/\odot has been replaced by G^2 as before and g^2 has been written for ϕ/ψ

Thus to establish the structure amplitudes on an absolute scale, and at the same time correct for absorption and temperature effects, it is necessary to find g as a function of $\sin \theta$. This can be done by the use of Equ. (1)

$$F_s - F_c = S(f_s - f_c)$$

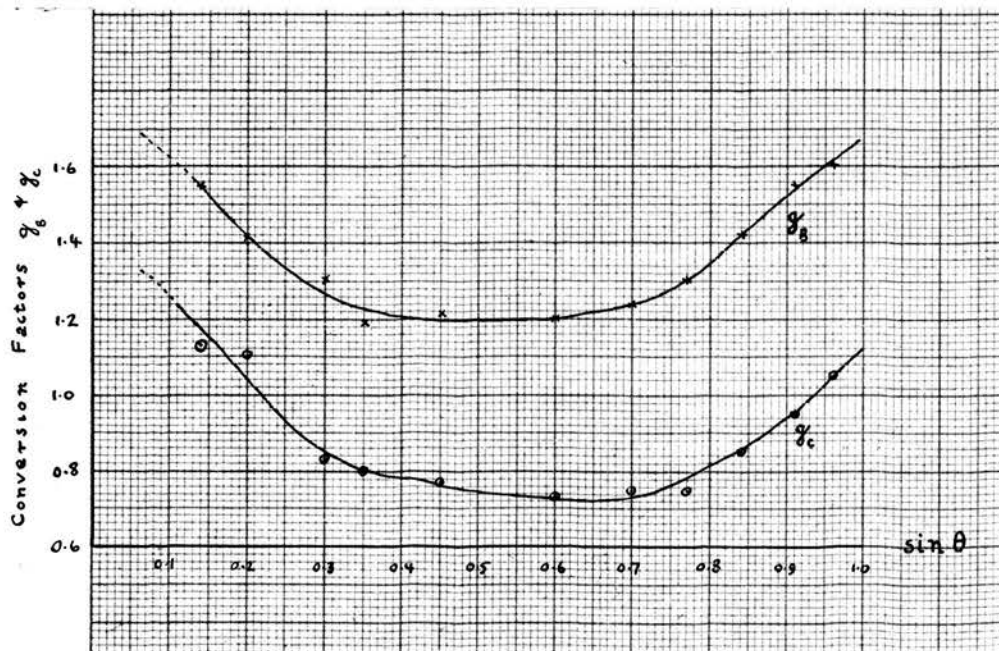
$$\text{i.e. } g_s G_s - g_c G_c = S(f_s - f_c)$$

The reflections were grouped together in about a dozen sets, all reflections belonging to one set having approximately the same value of $\sin \theta$. g_s and g_c could therefore be regarded as constant within each

group. Approximate values of g_s and g_c were obtained by inspection of a number of cases where one of G_s or G_c happened to be zero. These approximate values, when inserted in the equation above, were sufficient to establish the signs to be associated with $|G_s|$ and $|G_c|$ in the great majority of cases. More accurate values of g_s and g_c were then obtained by setting up a large number of simultaneous equations involving G 's of approximately the same Bragg angle and solving for g_s and g_c by the method of least squares.

g_s and g_c are shown as functions of $\sin \theta$ in Graph 4. The form of the curves bears out the statement of Bradley⁽¹⁸⁾ that for crystals of moderate absorption - co-efficient the absorption and temperature factors cancel one another out over most of the range.

Graph 4.



Each G_B and G_C was now multiplied by the appropriate value of g_B and g_C to give F_B and F_C . F 's of the type (h50) are given below as an example.

h	$S_B \times f_B$	$S_C \times f_C$	$\therefore (F_B - F_C)_{\text{calc.}}$	$G_B \times g_B$	$G_C \times g_C$	$\therefore (F_B - F_C)_{\text{obs.}}$
0	0	0	0	0	0	0
1	32	12	20	-30	-40	10
2	-44	-18	-26	-16	14	-30
3	-68	-28	-40	18	48	-30
4	60	24	36	-8	-48	40
5	62	30	32	44	20	24
6	-36	-20	-16	-94	-66	-28
7	-16	-16	0	± 56	± 58	± 2
8	-6	6	-12	8	14	-6
9	-34	-4	-30	-10	6	-16
10	42	10	32	60	26	34
11	60	20	40	22	0	22
12	-50	-20	-30	-48	-18	-30
13	-48	-24	-24	26	44	-18
14	26	18	8	-8	-22	14
15	8	18	-10	-58	-52	-6
16	12	-8	20	-26	-38	12
17	34	-2	36	16	-24	40
18	-38	-4	-34	-26	16	-42
19	-52	-12	-40	-36	12	-48
20	40	14	26	46	24	22
21	26	20	6	± 20	± 22	± 2
22	-16	-16	0	± 20	± 18	± 2
23	0	-16	16	0	-16	16
24	-14	10	-24	0	18	-18
25	-32	6	-38	-42	-20	-22

From this table it will be observed that:

- (1) The agreement between calculated and observed values of $F_B - F_C$ is good, the mean deviation being about 7. In some cases the deviations are greater that can be explained by experimental error (e.g. (11, 5, 0)) but there is no systematic deviation.

This is to be expected since the replacement of bromine by chlorine must cause small changes in the positions of the other atoms.

(2) Separate structure factors, S_B and S_C have been worked out for the bromine and chlorine atoms. This was done because it was found that if it was assumed that chlorine had exactly the same co-ordinates as bromine there was systematic deviation between calculated and observed values of $F_B - F_C$. A general improvement resulted if it was assumed that the chlorine had not the same x-co-ordinate as the bromine, but had instead $x = .058$. This was confirmed by evaluating the Patterson-Harker function

$$P(u \frac{1}{2}) = \sum_h \left\{ \sum_l (-1)^l F_C^2(h0l) \right\} \cos 2\pi hu$$

which was found to have a maximum at

$$u = \frac{1}{2} - 2x = 23 \cdot 1/60, \text{ giving } x = .0575.$$

y and z co-ordinates were found to be unchanged.

Separate structure factors were worked out when dealing with reflections of the type (hko) and (hol), but not (okl) since x-co-ordinates are not involved in the latter.

(3) The sign which is to be associated with the F's is quite clear in most cases, but is doubtful in others where the calculated value of $F_B - F_C$ is small (e.g. (5, 21, 0)) and quite uncertain in those for which the calculated difference is almost zero (e.g. (5, 7, 0)).

Electron density maps.

The electron density projected on (010) will be taken as an example. This is given by

$$\rho(xz) = 1/A \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} F(hol) \cos(2\pi hx + 2\pi lz - \alpha)$$

in the general case. In the particular case of space group $P2_12_12_1$ this reduces to

$$\begin{aligned} \rho(xz) = & 4/A \sum_{h=0}^N \sum_{l=0}^L F(hol) \cos 2\pi hx \cos 2\pi lz \\ & - 4/A \sum_{h=0}^N \sum_{l=0}^L F(hol) \sin 2\pi hx \sin 2\pi lz \end{aligned}$$

$h+l=2n$
 $h+l=2n+1$

the origin being taken on the centre of symmetry of the projection, which has co-ordinates $(0, \frac{1}{4})$ referred to the true unit cell origin.

ρ was computed at intervals of $1/60$ th of the crystallographic axes by means of the well-known Beavers-Lipson strips. Special strips were written out by hand for wave numbers greater than 20, since values of h up to 28 had to be dealt with. F_p 's were used rather than F_c 's in the final syntheses since the former appear to give the more accurate results; the approximate maps obtained by syntheses from which terms of doubtful sign had been omitted were generally worked out using both sets of structure amplitudes as co-efficients. Co-efficients were divided by a factor of four to facilitate computation, the loss in accuracy can be shown to be negligible.

The F 's were divided into four groups,

- | | |
|----------------------------|----------------------------|
| (1) $h + l$ even, h even | (2) $h + l$ even, h odd. |
| (3) $h + l$ odd, h even | (4) $h + l$ odd, h odd. |

Those of class (1) were used as co-efficients in a one-dimensional synthesis

$$\alpha(x, l) = \sum_0^H F_1(hol) \cos 2\pi hx$$

This gave a preliminary table containing values of α for sixteen values of x ($0/60, 1/60 \dots 15/60$) and six values of l ($0, 2, \dots, 10$)

Similar preliminary tables were evaluated which gave

$$\beta(x, l) = \sum_0^H F_2(hol) \cos 2\pi hx$$

$$\gamma(x, l) = \sum_0^H F_3(hol) \sin 2\pi hx$$

$$\delta(x, l) = \sum_0^H F_4(hol) \sin 2\pi hx$$

The electron density along the line $x = 1/60$ for example was then got by carrying out four final syntheses.

$$A(1/60, z) = \sum_0^L \alpha(1/60, l) \cos 2\pi lz$$

$$B(1/60, z) = \sum_0^L \beta(1/60, l) \cos 2\pi lz$$

$$C(1/60, z) = \sum_0^L \gamma(1/60, l) \sin 2\pi lz$$

$$D(1/60, z) = \sum_0^L \delta(1/60, l) \sin 2\pi lz$$

From the symmetry and antisymmetry about the origin of cosine and sine functions respectively it follows that $\rho(1/60, z)$ is given by:-

$$(A + B) - (C + D) \quad \text{between } z = 0/60 \text{ and } 15/60$$

$$(A - B) - (C - D) \quad " \quad z = 30/60 \quad " \quad 15/60$$

$$(A - B) + (C - D) \quad " \quad z = 30/60 \quad " \quad 45/60$$

$$(A + B) + (C + D) \quad " \quad z = 60/60 \quad " \quad 45/60$$

In this way values of ρ for the $60 \times 15 = 900$ points of the unique area were obtained.

The map obtained in this way is shown in Fig. 7.4. Fig. 7.3, which represents the result of a synthesis from which no terms were omitted (obtained later) is reproduced alongside for comparison.

Maps of the electron density projected on (100) and (001) were obtained in the same way.

Figs. 7.4 and 7.3

- 7.4 Approximation to electron density projected on (010)
- 7.3 Final map of electron density projected on (010) obtained later by other methods and reproduced at this point for comparison with 7.4.

The first contour is drawn at $4e./A^2$, thereafter contours are at an interval of $2e./A^2$ except in the bromine atom where the interval is $10e./A^2$.

FIGURE 7.3



FIGURE 7.4



CHAPTER 6.

DETERMINATION OF STRUCTURE.

The structure was by no means obvious from these maps, which were necessarily inaccurate because of the omission from the syntheses of terms whose signs were doubtful. The effect of omitting these terms can be seen by comparing Figs. 7.4 and 7.3; certain atomic positions are represented by diffuse or scattered peaks, while other peaks do not represent atomic positions. The sodium atom was readily located since it gives electron density maxima considerably greater than those due to carbon or oxygen atoms and it was known that its distance from the bromine atom would be approximately 2.9 Å.

The sucrose structure was arrived at in the following way. Copies of the electron density maps on a scale of 1" = 1Å. were supported by a wooden framework so as to represent three sides of the unit cell. Three electric lamps were arranged at a distance of several yards so that each gave an almost parallel beam of light perpendicular to one of the planes. An object held inside the model of the unit cell was thus projected on all three planes by means of the shadows cast. A number of

small spheres with holes bored to accommodate tetrahedrally disposed 'bonds' of steel rod 1.5" long were used to build up a molecular model, starting from a single atom and adding others in such a way that the shadows cast by the model fell on maxima of all three electron density maps. In this way a satisfactory structure was arrived at for one half of the molecule - the glucose residue. Considerable difficulty was experienced in settling the approximate configuration of the fructose residue since this approximately planar arrangement of atoms projects edgewise on (100) and (001) and is obscured by the other half of the molecule in the (010) projection. A number of arrangements were tried until one was found which gave satisfactory agreement between calculated and observed structure amplitudes. Values of all zero layer line structure amplitudes were calculated for this structure and thus the signs of terms previously omitted from the syntheses were found. The agreement between calculated and observed structure amplitudes is good, as can be seen from the following table, which gives a section chosen at random from the complete set of results. Values of the atomic scattering factors were taken from Bragg, 'The Crystalline State' p. 328, and no distinction was made between C, CH and CH₂ or between O, OH and H₂O. A complete set of calculated and observed F's has not been reproduced here, but all

the information contained in such a table has been presented in another form (see later).

Example of calculated and observed F's

k = 1	h	F calc.	F obs.	k = 2	h	F calc.	F obs.
	0	0	0		0	- 2	14
	1	34	28		1	-38	-54
	2	92	80		2	- 8	-14
	3	- 6	6		3	-84	-80
	4	-38	-46		4	- 8	-16
	5	-24	-20		5	0	12
	6	100	108		6	-86	-64
	7	- 8	± 18		7	76	72
	8	2	24		8	-36	-44
	9	50	68		9	-50	-34
	10	-106	-92		10	-32	-38
	11	56	58		11	34	± 32
	12	40	28		12	16	± 30
	13	34	± 26		13	14	28
	14	-10	-18		14	38	34
	15	4	16		15	-56	-56
	16	-14	-20		16	-50	-42
	17	6	8		17	72	56
	18	76	68		18	38	± 26
	19	- 4	- 8		19	-18	0
	20	-44	-38		20	- 2	0
	21	34	32		21	-26	-30
	22	- 4	± 16		22	20	24
	23	-22	-12		23	64	54
	24	20	18		24	66	48
	25	-26	-28		25	-14	-14
	26	-52	-48		26	-22	-18
	27	54	40		27	16	18
	28	52	34				

The electron density maps were now recalculated, all F's observable with CuK_α radiation being included in the syntheses. The unique area of these maps in the case of the projections on (010)

and (001) is shown in Figs. 7.3 and 8.3. Fig. 9.3 shows the complete map of the electron density projected on (100); in this case the four molecules of the unit cell are projected on to an area of $9.27 \times 8.43 = 82 \text{ \AA}^2$, so that very few atoms are separately resolved. Final atomic co-ordinates were therefore derived almost entirely from the projections on (010) and (001).

Parameters of the structure.

The structure is defined by 81 parameters, and is therefore as complex as any which have been successfully investigated by X-ray methods.

The atoms have been numbered in accordance with Fig. 10.1. The co-ordinates refer to that molecule of the four contained in the unit cell which is contained approximately within the planes $x = \frac{1}{2}$ and $x = \frac{3}{4}$, since the sucrose molecule contained in this quarter of the unit cell can be more readily visualised in terms of the structural formula. Parameters are in sixtieths of the cell edges

Atom	x	y	z
Br	33.9	19.4	56.9
Na	34.4	1.7	52.5
W1	40.6	6.5	46.0
W2	37.9	49.3	55.0
O1	40.3	23.7	18.0
O2	46.2	13.4	14.2
O3	42.3	59.8	8.2
O4	34.4	0.0	11.0
O5	38.1	14.2	29.8
O6	33.3	2.0	35.5
O1 ¹	45.8	41.7	26.2
O2 ¹	39.5	33.0	31.4
O3 ¹	38.4	36.0	6.5
O4 ¹	33.0	45.5	19.2
O6 ¹	31.8	29.2	37.1
C1	41.2	17.2	24.0
C2	43.2	10.8	18.5
C3	40.4	6.5	12.4
C4	37.2	3.5	17.0
C5	35.4	11.0	22.7
C6	32.0	8.0	29.0
C1 ¹	45.0	34.0	22.0
C2 ¹	40.9	32.0	22.0
C3 ¹	38.5	37.2	16.6
C4 ¹	35.2	38.2	22.2
C5 ¹	36.5	38.6	31.9
C6 ¹	34.0	35.9	38.9

Description of Sucrose molecule.

Figs. 7.1, 8.1 and 9.1 show single "molecules" of Suc. NaBr. $2H_2O$ projected on (010), (001) and (100) respectively. In Fig. 10.3 the observed valency bonds and angles of the sucrose molecule are shown. The two halves of the molecule have been separated in order to clarify the diagram.

The oxygen atoms attached to carbons 1 and 2 of the pyranose ring (O1 and O2) are in cis positions, as are those on carbon atoms 2 and 3 of the furanose ring (O1 and O3¹). This establishes the fact that the glucose residue possesses the α -configuration while the fructose residue possesses the β -configuration, so that sucrose may be described as

1- α - glucopyranose - 2- β - fructofuranose.

The pyranose ring is identical, within the limits of experimental error, with the Sachse trans form shown in Fig. 1.1. The mean C-C distance within the ring is 1.51 Å, which is sufficiently close to the accepted value. The oxygen atom of the ring is not distinguished from the carbons by either its bond lengths or angle, and the same may be said of the oxygen atom of the furanose ring. All the bond angles of the glucose residue may be regarded as tetrahedral, the mean value being 108° and mean deviation from the tetrahedral angle 4° . 4° may therefore be taken as a measure of the probable error to which the observed angles are subject.

The fructose residue possesses some unexpected features. The five atoms of the furanose ring are definitely not coplanar, but the departure from planarity is in the interests of a more general planarity of the residue as a whole. Fig. 10.2 shows how carbon atoms 3, 4 and 5 ($C3^1$, $C4^1$ and $C5^1$ of the diagrams) are "staggered" within the ring in such a way as to bring their attached OH and CH_2OH groups more nearly into the mean plane of the ring. The angles which the valency bonds of the hydroxyls $O3^1$ and $O4^1$ make with the adjacent ring bonds are definitely high at 115° , 118° , 116° and 113° , the departure from the normal value of $109\frac{1}{2}^\circ$ is again in such a direction as to bring the addenda into the mean plane of the ring. The average bond angle within the ring is 104° , C-C distances within the ring are definitely lower than the normal aliphatic C-C distance of 1.54 A., the average being in fact 1.44 A. Deviations, from the average are very small in this case, but this may be a coincidence.

The average C-C distance outside the rings is 1.51 A., the average C-OH distance 1.42 A. The mean deviation of individual bond lengths of one type from the average of that type is 0.03 A., this may be taken as the probable error to which measured bond lengths are subject. The maximum possible error is

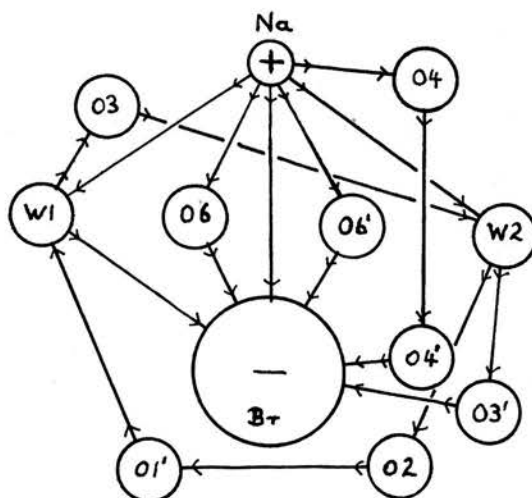
thought to be about 0.1 Å. To establish bond lengths and angles with greater accuracy would require three-dimensional methods, since some atoms (e.g. O6, O6¹) are not resolved from other atoms in any of the three projections.

Description of Structure.

Fig. 10.1 shows the contents of one unit cell projected on (001). Both sodium and bromine have co-ordination groups of six, but the grouping around the sodium cation is much more regular than around the larger bromine anion. Sodium has links to bromine, two water molecules and three hydroxyls while bromine has links to sodium, one water molecule and four hydroxyls. If bonds are regarded as being directed from positive to negative regions of the structure each hydroxyl has one incoming and one outgoing bond while each water molecule has two incoming and two outgoing bonds, these bonds being of strength 1/6 if it is assumed that the six sodium bonds are of equal strength, as seems likely in view of the fact that any two of the six are either almost mutually perpendicular or in the same straight line. This is in agreement with the concept of polarised OH groups and the Bernal-Fowler model of the water molecule, except that the distribution of water molecule bonds cannot be said to be tetrahedral.

In the case of water molecule 2 (W2) it is approximately so, but the four bonds of W1 are more nearly coplanar than tetrahedrally disposed. Bonds (other than valency bonds within the sucrose molecule) are shown by the dotted lines of Fig. 10.1. It will be seen that the sodium and bromine ions and the water molecules play a very important part in linking the sucrose molecules together. There are in fact only two direct OH-OH bonds between adjacent sucrose molecules in the structure ($O2 - O1^1$ and $O4 - O4^1$), the remaining hydroxyls may be regarded as linked through the medium of the ions and water molecules. In this way bond-chains are formed which run throughout the structure. These can be seen in Fig. 10.1, apart from those which run perpendicular to the plane of the diagram in the direction of the c-axis. One such chain in the direction of the b-axis is shown by the red lines. The linkages between the various charged and polarised groups can be summarised in a schematic diagram.

Fig. 10.4.



This diagram involves the sodium and bromine ions, eight hydroxyl groups and two water molecules of each "molecule" of $\text{Suc. Na.Br. } 2\text{H}_2\text{O}$ which take part in bonding of this type. In this diagram no distinction is possible between atoms which occupy equivalent positions (identical positions within different molecules). Thus for instance the bond shown as passing from sodium via O6^1 to bromine, actually passes from sodium via the hydroxyl to an adjacent bromine to which the sodium is not directly linked. The schematic diagram is of value in drawing attention to one particular point. The bonds of the "ring" $\text{W}_1\text{O}_3\text{W}_2\text{O}_2\text{O}_1\text{W}_1$, which corresponds in the three-dimensional structure to a spiral of infinite extent in the direction of the c-axis, could be reversed to run $\text{W}_1\text{O}_1\text{O}_2\text{W}_2\text{O}_3\text{W}_1$ and the necessary conditions would appear to be equally well fulfilled. This is of interest because a similar reversible bond chain in Rochelle salt (sodium potassium tartrate tetrahydrate) has been suggested by Beevers and Hughes⁽¹⁹⁾ as an explanation of the abnormal dielectric properties of that substance. An investigation of the dielectric properties of sodium bromide sucrate will be made at the first opportunity. Bond lengths of the structure are summarised below.

Type	Observed lengths	Average	Sum of radii.
OH-OH	2.66, 2.77	2.71	2.66
OH-Na	2.32, 2.42, 2.62,	2.45	2.31
Na-H ₂ O	2.41, 2.56	2.48	2.31
OH-Br	3.22, 3.24, 3.28, 3.31, 3.50		3.28
Br-H ₂ O	3.59	3.59	3.28
H ₂ O-OH	2.67, 2.70, 2.73, 2.99, 3.00	2.82	2.66
Na-Br	2.93	2.93	2.93

The radii of sodium and bromine have been taken as 0.98 and 1.95 A. respectively, OH and H₂O have been given the oxygen radius of 1.33 A. The effective radius of a water molecule in this structure appears to be somewhat greater than this at about 1.5 A.

Water molecule 1 is only 2.76 A. distant from O5, the oxygen atom of the pyranose ring, but this has not been regarded as a bond since the water molecule already has four bonds and it seems unlikely that this oxygen atom should possess other than primary bonds. Certainly the oxygen atom which is common to the two residues and that which is a member of the furanose ring are linked to carbon atoms only.

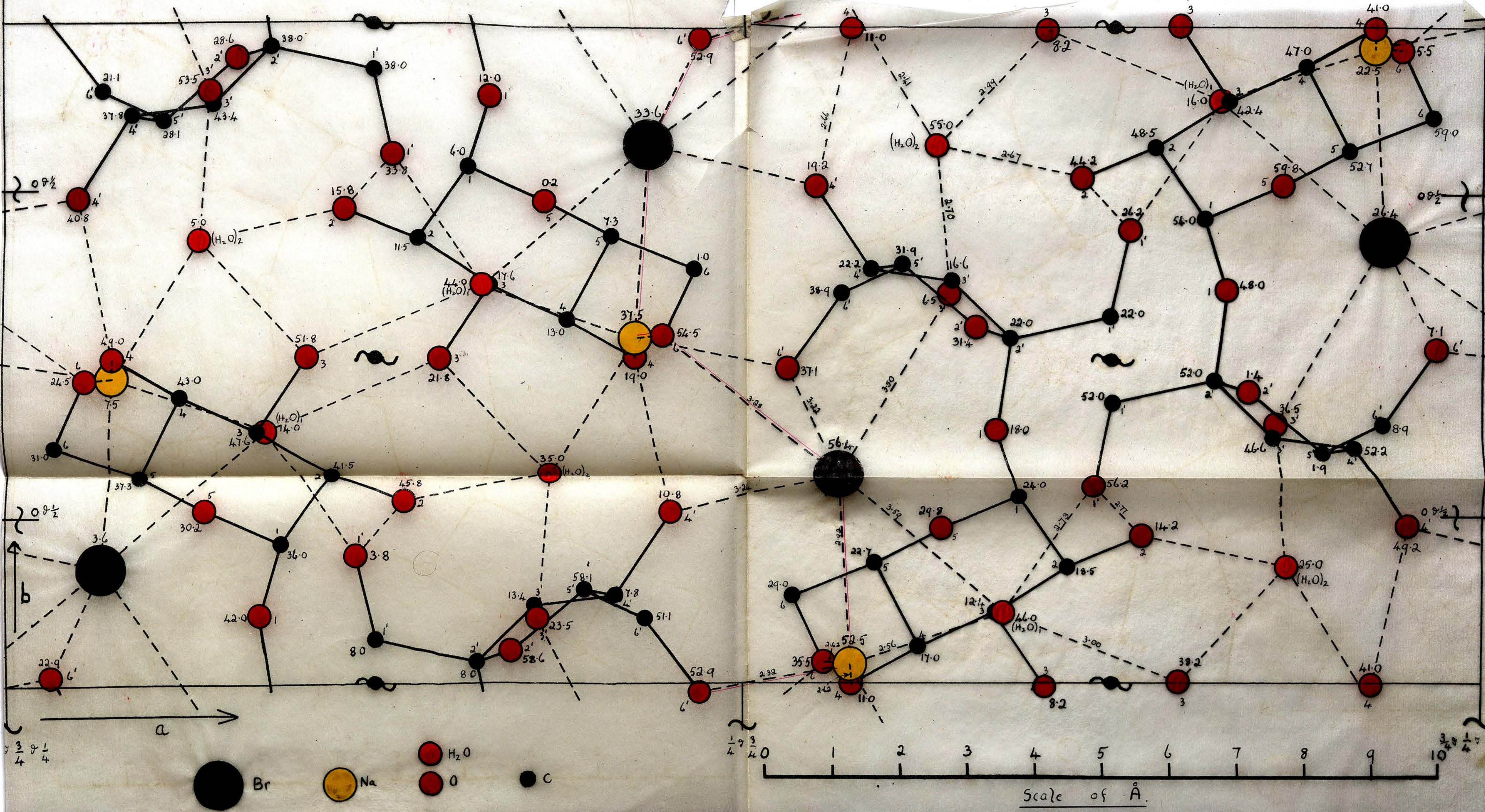


Fig. 10.1

Contents of unit cell projected on (001)

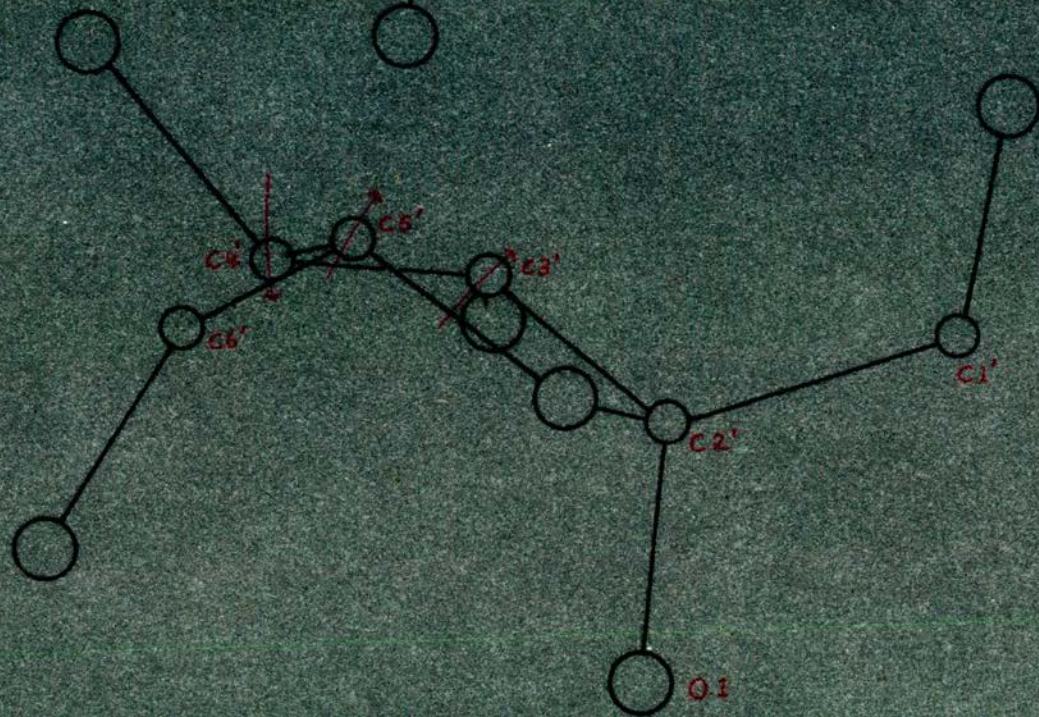
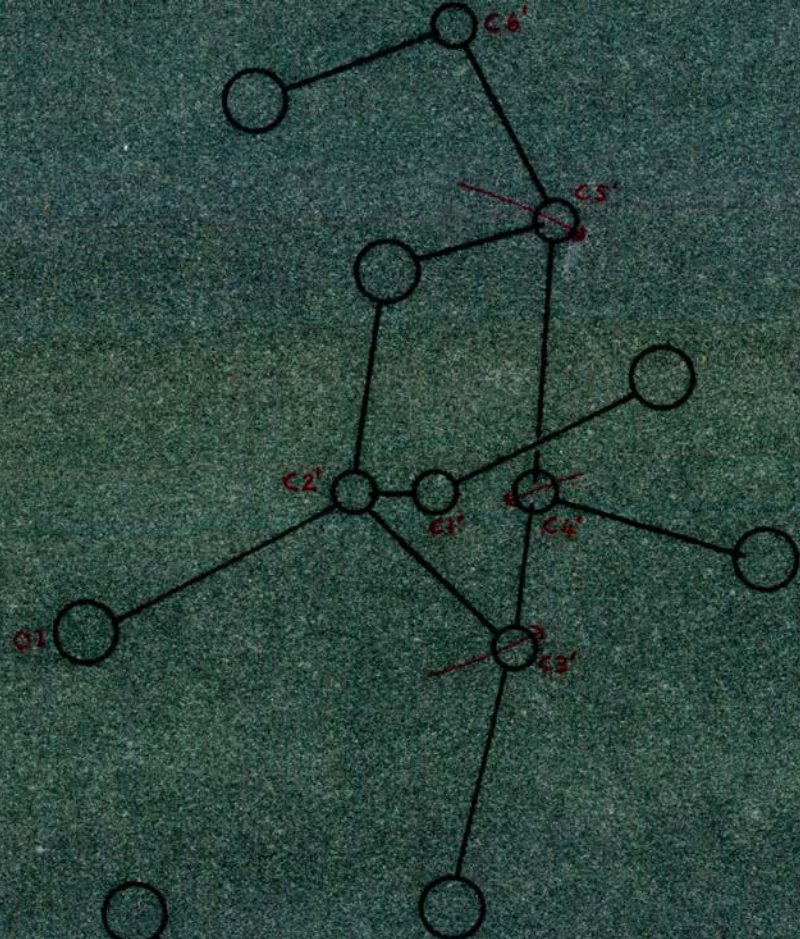
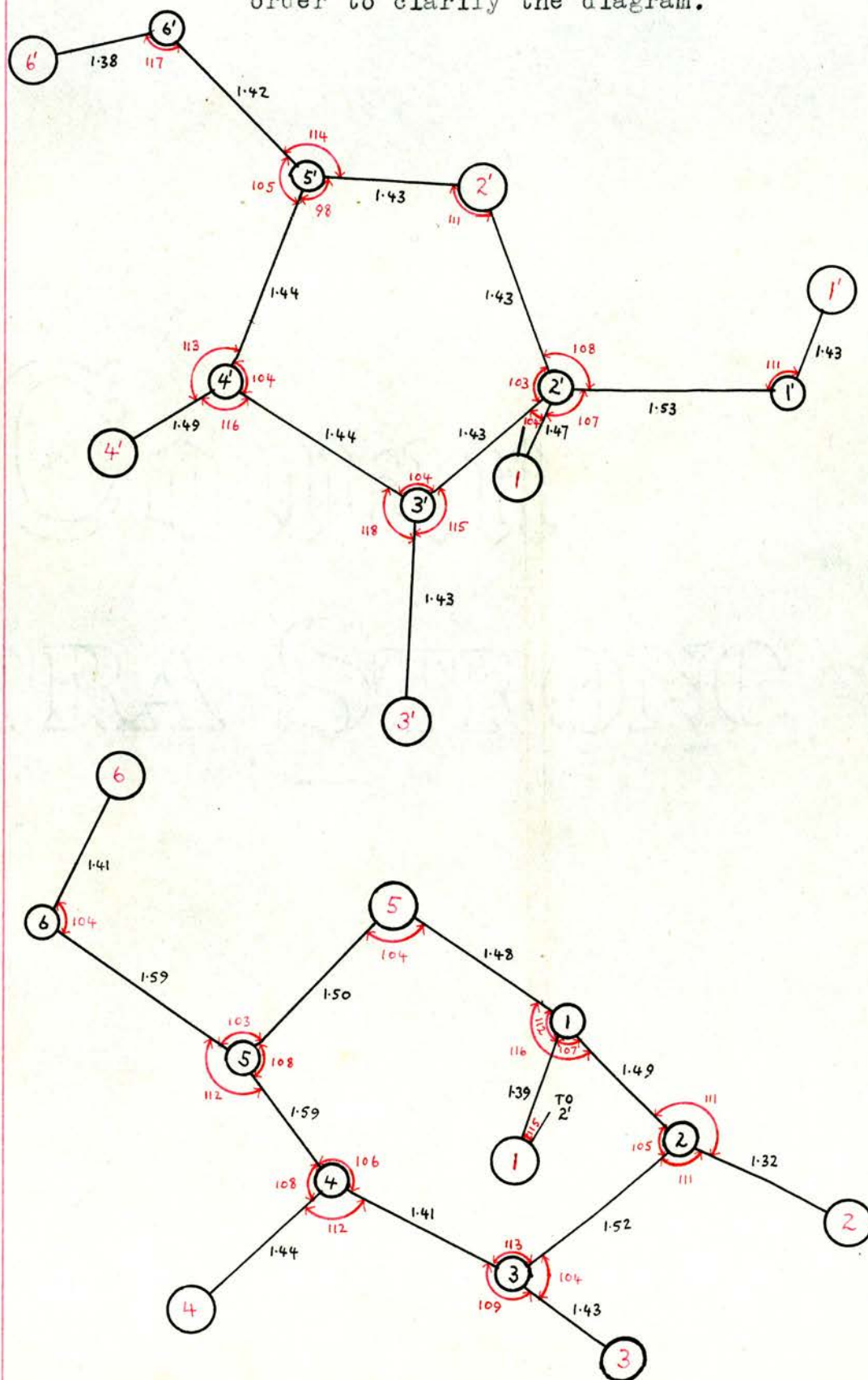


Fig. 10.2

Fructose residue projected on two perpendicular planes.

Fig. 10.3

Bond lengths and angles of the sucrose molecule.
The two halves of the molecule have been separated in
order to clarify the diagram.



CHAPTER 7.

DISCUSSION.

The question arises as to whether the structure described in the previous chapter is the only one consistent with the X-ray data. The method usually adopted in order to show that a postulated structure is the correct one consists in the presentation of tables of calculated and observed structure amplitudes. A section selected at random from such a table has been given in a previous chapter, the agreement between calculated and observed F's is good but is not such as to afford in itself convincing proof of the correctness of the structure. In crystals containing both heavy and light atoms the latter may be moved appreciably without altering radically the calculated structure amplitudes, there is thus a possibility that discrepancies thought to be due to experimental error may be due to completely wrong placing of one or more light atoms. Wyckoff (Structure of Crystals) cites cases in which alternative structures have been proposed for this reason. It is true that in this case the postulated structure fulfills certain stereochemical and other conditions, but it may be enquired how far

the final result is independent of all such considerations.

By presenting the calculated and observed structure amplitudes as their Fourier transforms, i.e. by comparing calculated and observed electron densities, convincing proof of the correctness of the structure may be obtained. This method possesses certain other advantages:-

- (1) It is unnecessary to recalculate the F's each time a parameter is changed by a small amount, all that is necessary is a change in the position of some of the contours of the calculated electron density map. A number of changes have in fact been made from the parameters on which the calculated F's were based.
- (2) Comparison of observed and calculated electron density maps indicates which atoms should be moved, and by how much, in order to make the calculated and observed results agree more exactly. Disagreement between calculated and observed F's merely indicates that adjustment of parameters is necessary without indicating which atoms are to be moved or the magnitude and direction of the changes, except in the case of a structure involving few parameters.
- (3) The theoretical electron density of a postulated structure may be derived by a direct method, the amount of computation involved is much less than in calculating structure factors.

That the electron density of a given structure may be derived directly from a knowledge of the atomic co-ordinates seems obvious in view of the fact that the electron distribution within isolated atoms is known and is approximately unchanged by chemical combination, but it must be borne in mind that there would be little point in comparing the observed distribution in an isolated atom with that of the Hartree model since observations made with radiation of wavelength 1.54 Å. do not give the true electronic distribution within the atom. The distribution, as calculated by a Fourier synthesis which contains only those F 's observable with $\text{CuK}\alpha$ radiation, is that of an imaginary atom which has the same atomic scattering factor as the real atom up to a certain limit ($\frac{\sin \theta}{\lambda} \approx 0.7$), after which its scattering factor is zero. This is a more diffuse distribution than actually obtains, and particularly in the case of heavy atoms it is not a distribution that falls continuously from a central maximum to zero but one which after a certain distance from the central maximum alternates between positive and negative values. This emphasises the point that the electron density observed with X-radiation is apparent only, since the real electron density can never be negative.

The apparent distribution in carbon, for example, was found by considering a carbon atom at the

point $(0, \frac{1}{4}, 0)$ in a unit cell of the same dimensions and space group as that of sodium bromide succrate.

The point $(\frac{1}{4}, 0)$ is a centre of symmetry of the projection on (100) and was taken as the origin.

The electron density projected on (100) is given by

$$\rho(yz) = 4/A \sum_k \sum_l F(okl) \cos 2\pi ky \cos 2\pi lz$$

But since the scattering matter consists of a single atom at the origin of the projection together with three identical atoms at the equivalent points $(0,0)$, $(\frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2})$ of the projection we have

$$F(okl) = 4f \text{ when } k+l \text{ is even.}$$

$$= 0 \text{ when } k+l \text{ is odd.}$$

$$\therefore \rho(yz) = 16/A \sum_k \sum_l f \cos 2\pi ky \cos 2\pi lz$$

$$\text{and } \rho(yo) = 16/A \sum_k \left\{ \sum_l f \right\} \cos 2\pi ky$$

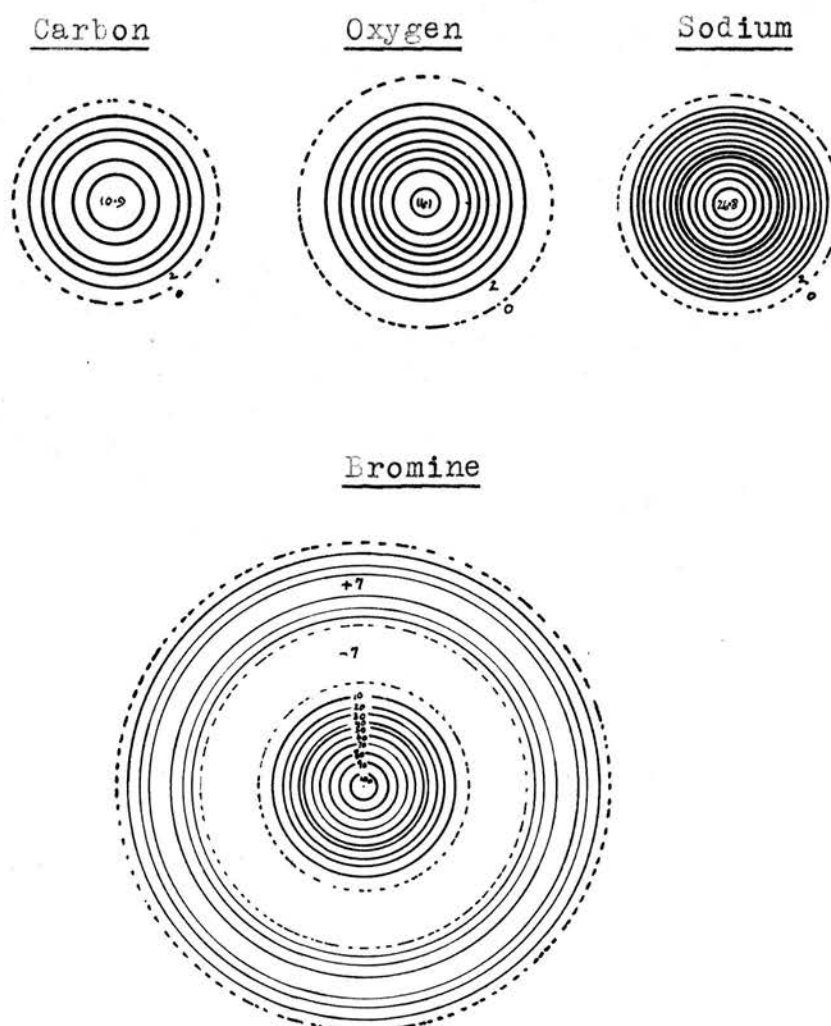
This represents a section through twice the projected electron density of a carbon atom since the two atoms at $(0,0,0)$ and $(\frac{1}{2}, 0, 0)$ coincide at the origin in a projection on (100). Hence the electron density along a line passing through the centre of the projection of a single carbon atom is given by

$$\rho(yo) = 8/A \sum_k \left\{ \sum_l f \right\} \cos 2\pi ky$$

The corresponding value of f was written beside each point of the relevant section of the reciprocal lattice which had $k+l$ even and the f 's for all points having the same value of l were added.

The sums were then used as co-efficients in a one-dimensional Fourier synthesis, giving the electron density (apart from the numerical factor $8/A$) at points separated by $1/60$ th of the b-axis. Since atoms are spherically symmetrical the electron density will be the same at all points equidistant from the origin. The apparent distribution in carbon, oxygen, sodium and bromine was obtained in this way and is shown below.

Fig. 11.1.



It may be noted that the maximum electron density of an atom is proportional to the mean value of its scattering factor over the range within which observations can be made. It has been found in practice that the maximum electron density gives a more accurate means of distinguishing carbon, oxygen and sodium atoms than does the number of ^{electrons} ~~atoms~~ contained in the peak. One reason for this is that while the number of electrons in these atoms are in the ratio 1:1.33:1.67, their (apparent) maximum electron densities are in the ratio 1:1.5:2.5.

The following table shows the observed maximum electron densities for those atoms which give clear projections on (001) and (010). (Practically none of the atoms is separately resolved in the (100) projection). In those cases in which the atomic centre does not coincide with a point at which the electron density has been calculated the maximum electron density was obtained by graphical interpolation. A gap in the table indicates that the atom is not separately resolved in that projection.

<u>Atom</u>	<u>Max. e.d. on (001)</u>	<u>Max. e.d. on (010)</u>
01	15.7 e./Å ²	- e./Å ²
02	16.5	18.5
03	16.9	16.5
04	-	17.3
05	18.0	-
01 ¹	16.1	16.5
03 ¹	-	17.3
04 ¹	16.5	16.0
06 ¹	16.5	-
C1	12.7	-
C2	11.6	13.0
C3	-	13.0
C4	12.0	-
C5	10.1	-
C6	9.4	10.4
C1 ¹	12.7	-
C6 ¹	12.3	-
W1	-	14.7
W2	13.9	13.0
Br	90.0	95.0

The average maximum electron densities are 16.8, 13.9 and 11.7 e./A² for oxygen atoms, water molecules and carbon atoms respectively, the mean deviation from the average being 0.8 e./A² and the maximum deviation (C6 on (001)) 2.3 e./A². The calculated values are (if no account is taken of hydrogen)

	16.1	e./A ²	for oxygen
	16.1	" "	water
	10.9	" "	carbon
	100.0	" "	bromine
and	26.8	" "	sodium

The average value of the "background" electron density is + 1.3 e./A² and the mean deviation from the average 1.0 e./A². The theoretical electron density in the background is of course zero, points in the immediate neighbourhood of the bromine atom being excluded because of the diffraction effects which occur. The fact that the observed background is more often positive than negative indicates that the F's have not been established on exactly the absolute scale, but very nearly so. These results indicate that the observed electron density at any point of the (001) or (010) projections is subject to a probable error of the order of magnitude 1 e./A². The maximum error must be about 4 e./A² since small "ghost" maxima of this height occur. The observed electron density of the water molecules is thus

consistently lower than the value calculated for an oxygen atom by an amount which is rather greater than the experimental error. It is suggested that this is due to the fact that the water molecules have a greater thermal movement than the other atoms. This seems a plausible assumption in view of the fact that the water molecules are not attached to any other atoms by valency bonds. The assumption that all the units have the same temperature factor is implicit in the method of correcting for the temperature effect, thus any unit having thermal vibration greater than the average would have a maximum electron density less than the calculated value.

In Figs. 7.2, 7.3 and 8.2, 8.3 the calculated electron densities at all points of the unique areas of the (010) and (001) projections are compared with the observed values. (The calculated electron density has not been derived for the (100) projection because of the difficulties caused by molecular overlapping). It will be seen that not only are the maximum electron densities in good agreement but the electronic distribution and course pursued by the contour lines are very similar in both.

It may therefore be claimed that the structure described in the previous chapter is based on the X-ray data and is independent of stereochemical assumptions.

Fig. 7.1.

Structure projected on unique area of (010).

Fig. 7.2.

Calculated electron density of this structure.

Fig. 7.3.

Observed electron density on unique area of (010).

First contour at 4 e./\AA^2 , thereafter at an interval of 2 e./\AA^2 except in bromine where the interval is 10 e./\AA^2 .

FIGURE 7-1

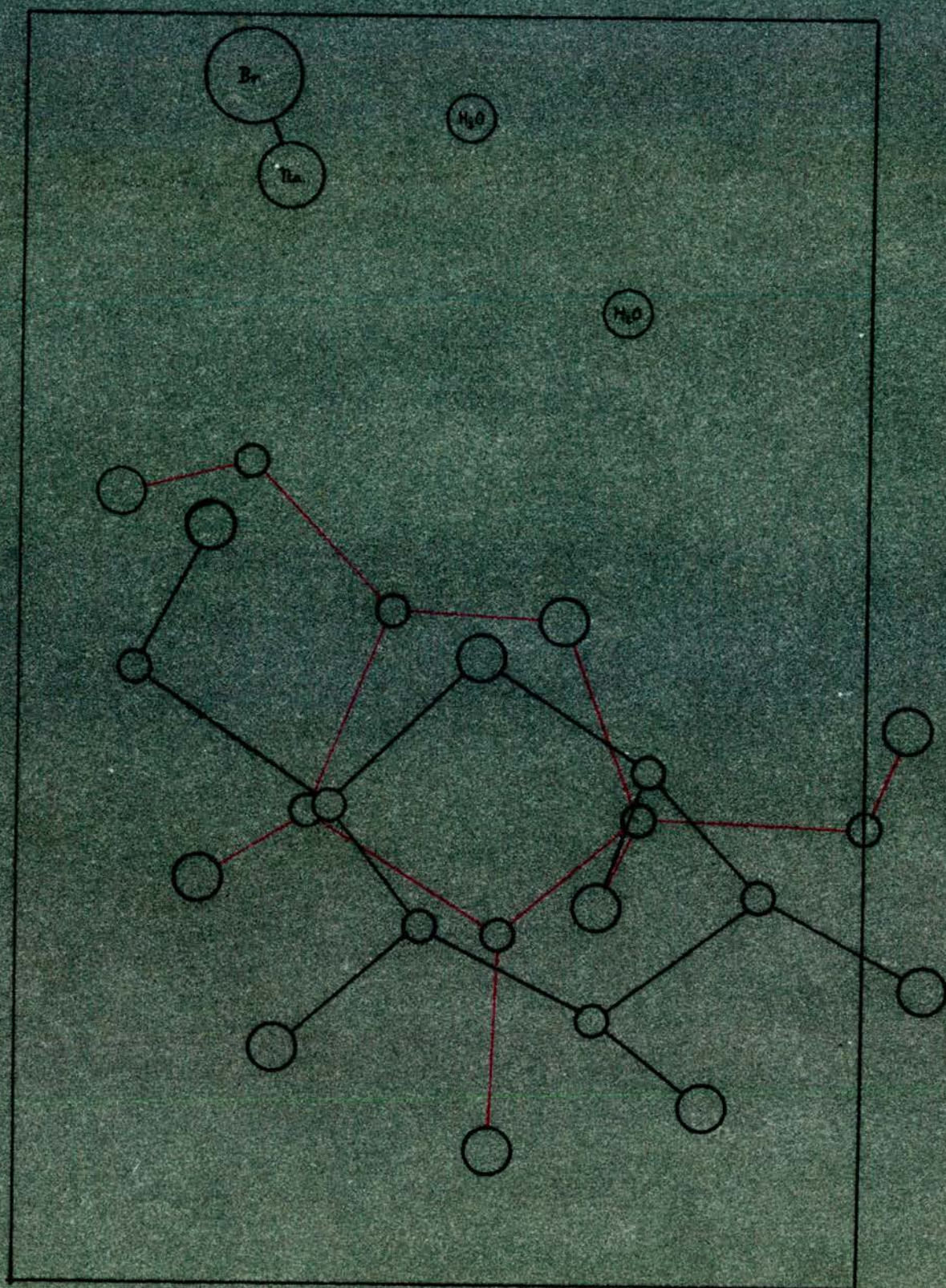


FIGURE 7.2



FIGURE 7.3



Fig. 8.1.

Structure projected on (001).

Fig. 8.2.

Calculated electron density of this structure.

Fig. 8.3.

Observed electron density on unique area of (001).

Contours as in Fig. 7.

FIGURE 8-1

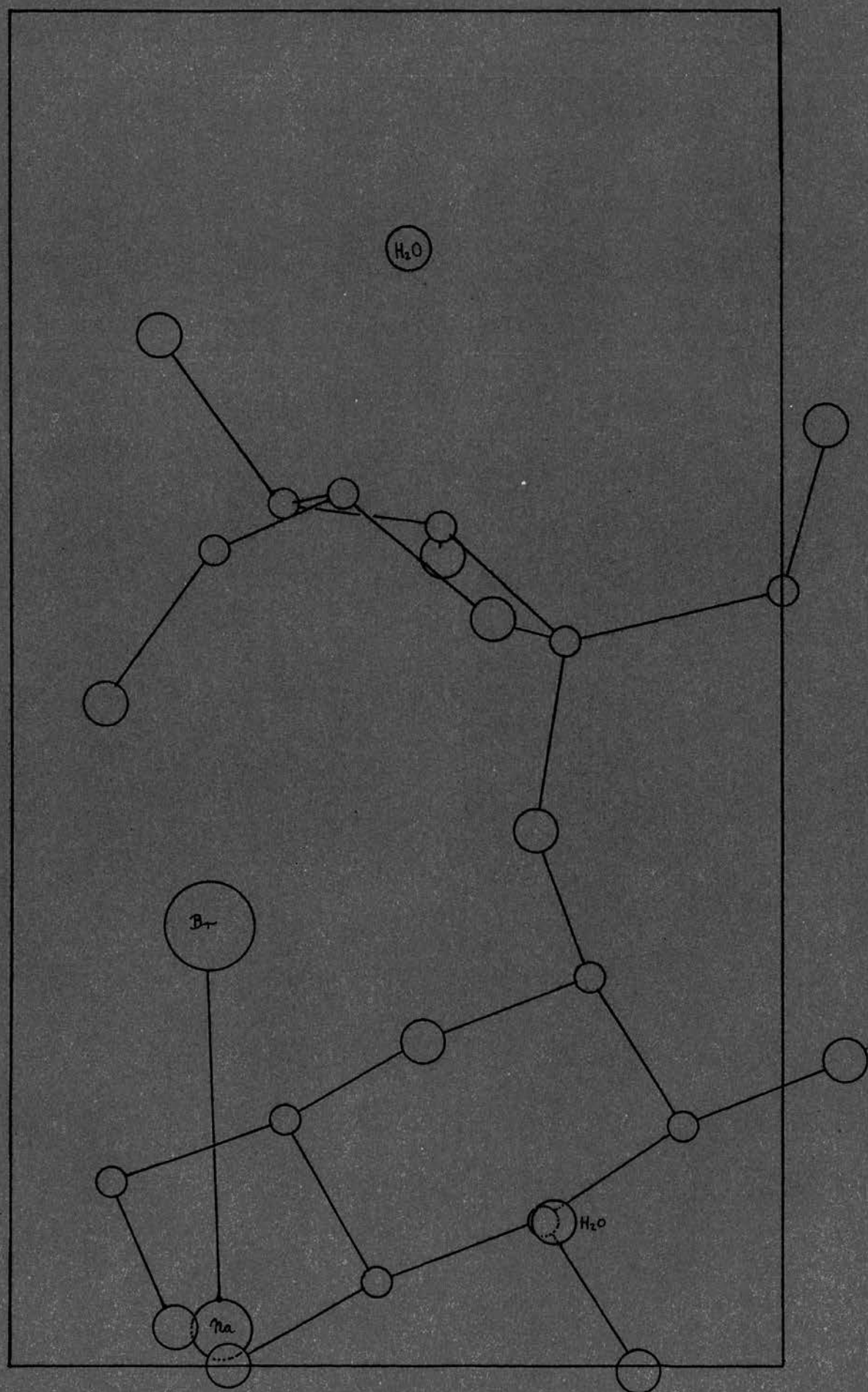


FIGURE 8.2

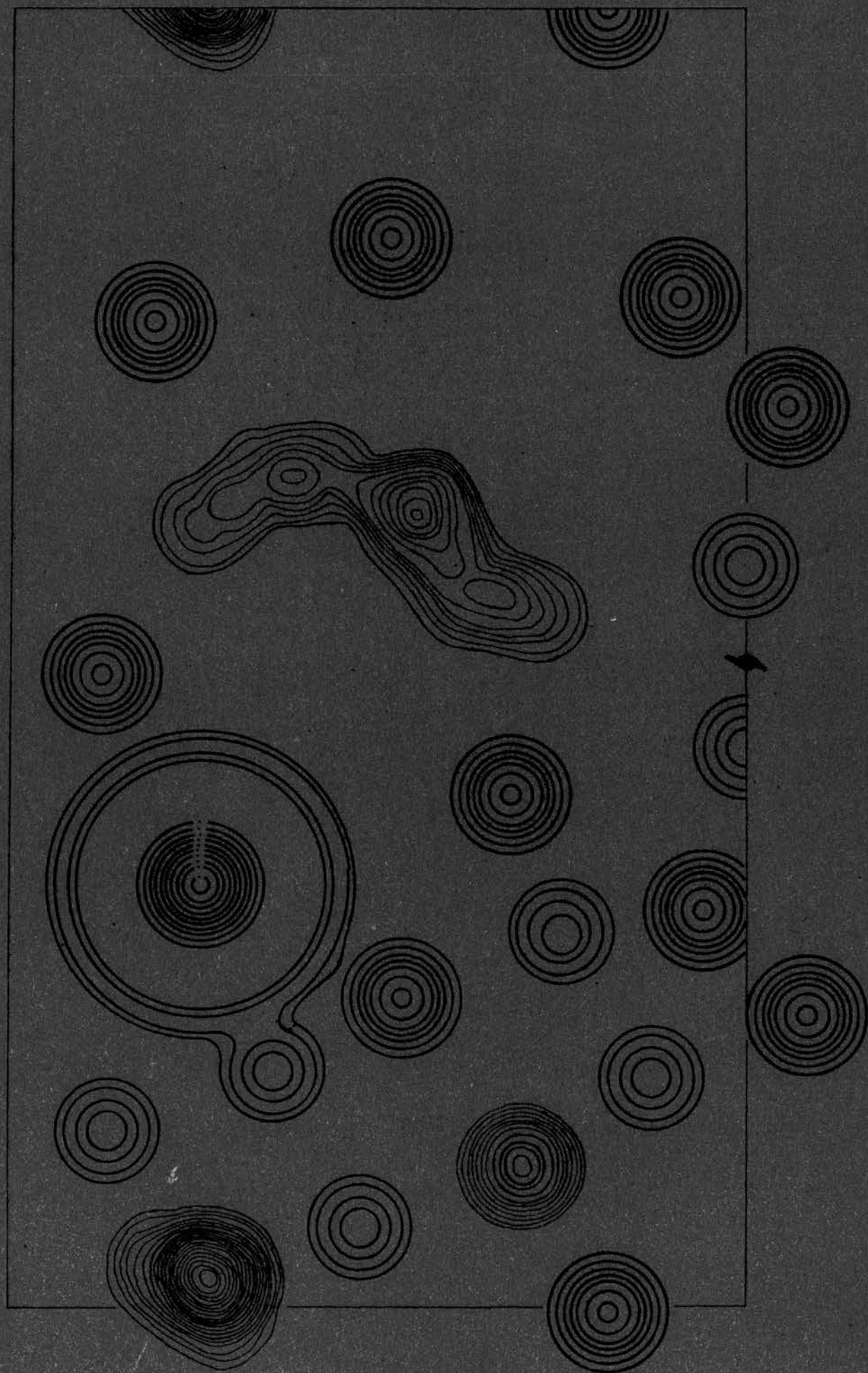


FIGURE 8.3

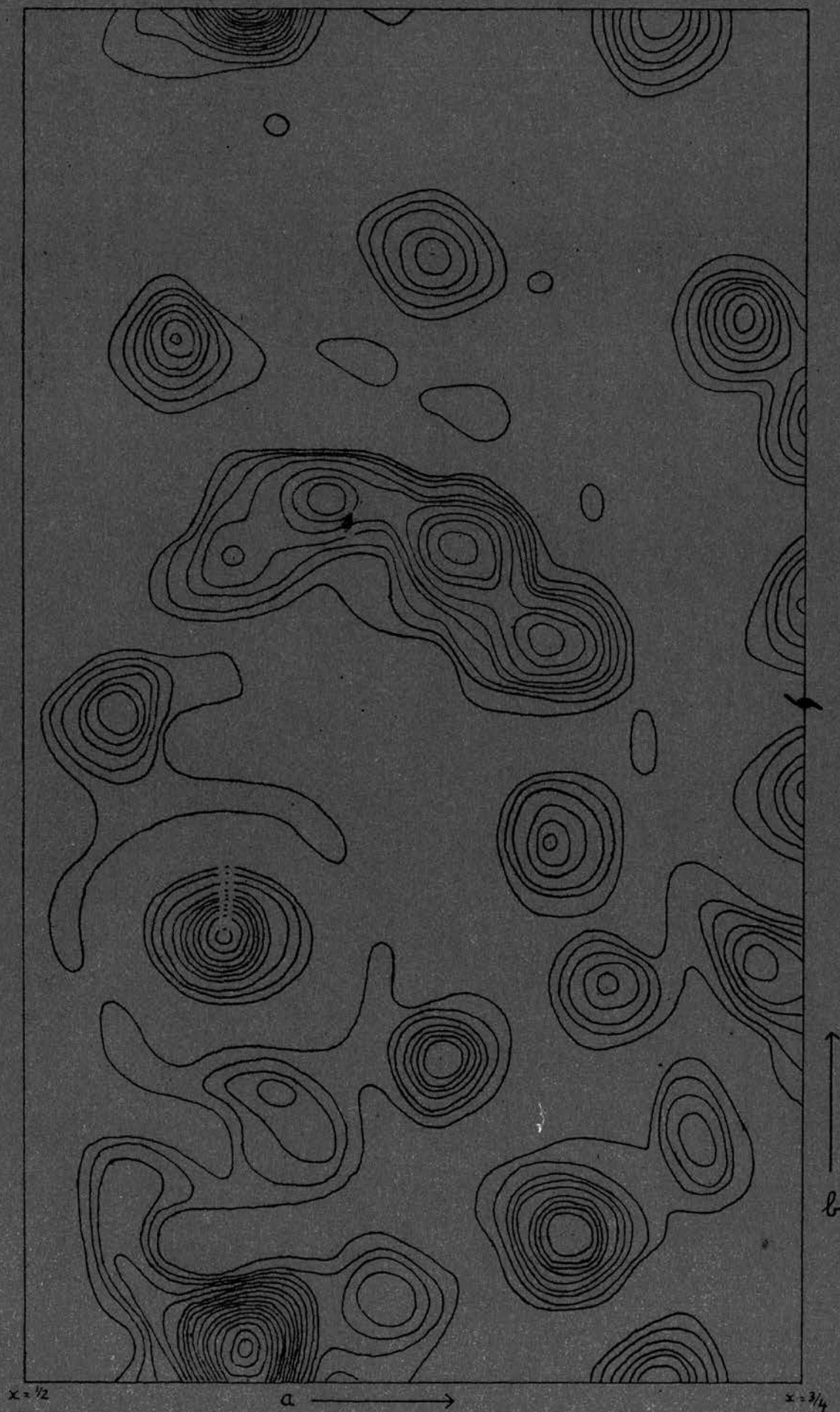


Fig. 9.1.

Structure projected on (100). (Only one molecule shown).

Fig. 9.3.

Observed electron density on (100).

First contour at 4 e./\AA^2 , thereafter at an interval of 4 e./\AA^2 except in bromine where the interval is 10 e./\AA^2 . Areas where the electron density is less than 4 e./\AA^2 are shown dotted.

FIGURE 9.1

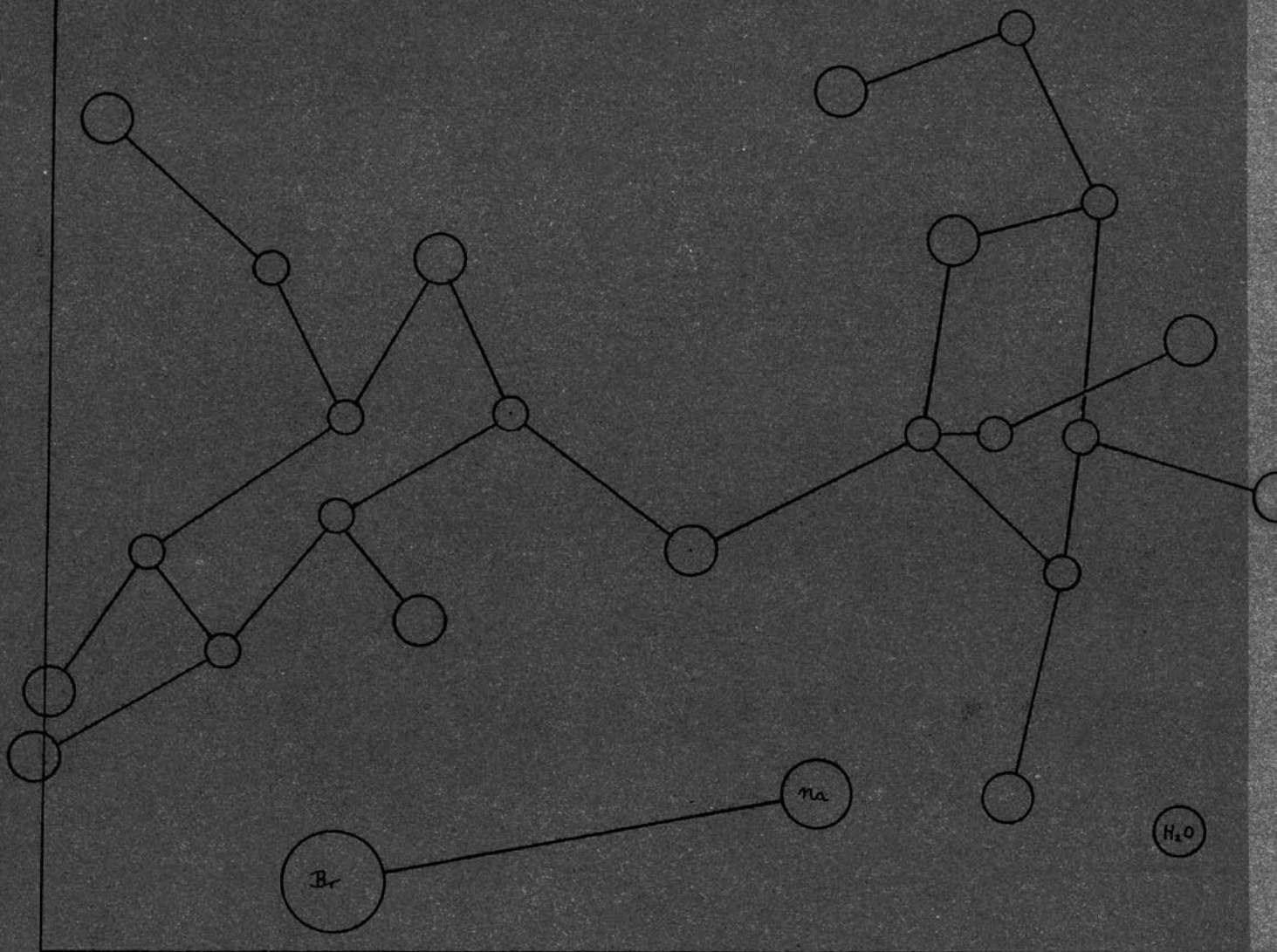


FIGURE 93



SUMMARY.

An investigation of the isomorphous substances $C_{12}H_{22}O_{11} \cdot Na Br \cdot 2H_2O$ and $C_{12}H_{22}O_{11} \cdot Na Cl \cdot 2H_2O$ has been made by the methods of X-ray crystallography.

The complete crystal structure of sodium bromide sucrate has been determined by Patterson and Fourier methods. It is shown that the pyranose ring, as it occurs in sucrose, is of the Sachse trans form and that the five atoms comprising the furanose ring are not coplanar but are arranged in such a way that the groups attached to the ring atoms are more nearly in the mean plane of the ring. Direct proof that sucrose may be described as

1 - α - glucopyranose - 2 - β - fructofuranose has been obtained for the first time.

Proof that the structure postulated is the correct one has been presented in a manner which is thought to have certain advantages over the customary method and on the basis of a comparison of observed and calculated electron densities it is claimed that the X-ray data is sufficient to establish the correctness of the structure independently of stereochemical assumptions.

In conclusion the author wishes to express his deep appreciation of the advice and encouragement given by Dr. C.A. Beevers throughout the course of this work.

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